

Torrefaction as a potential pretreatment for biomass saccharification

P. Brachi¹, A. Procentese¹, G. Ruoppolo¹, M. E. Russo¹, A. Marzocchella², R. Chirone¹

¹*Istituto di Ricerche sulla Combustione - Consiglio Nazionale delle Ricerche, P.le V. Tecchio 80, 80125 Napoli – Italy*

²*Dipartimento di Ingegneria Chimica dei Materiali e della Produzione Industriale - Università degli Studi di Napoli Federico II, P.le V. Tecchio 80, 80125 Napoli – Italy*

Introduction

Recently the use of lignocellulosic feedstock as source of fermentable sugars has been extensively investigated in order to develop biorefinery processes to produce liquid biofuels and bio-commodities. In particular, second generation biofuels have been proposed as the result of the conversion of sugars from residual biomass such as agriculture and food industry by-products. An example of liquid biofuel produced through sugar-based biorefinery is bio-butanol [1]. The possibility to produce butanol from low cost feedstocks, such as lignocellulosic food wastes, has been recently explored [2]. This process, as well as all the second generation biorefinery processes, asks for physical or chemical pretreatments of the lignocellulose (e.g., acid hydrolysis, alkaline wet oxidation and steam explosion) in order to mitigate the hindrance effect of lignin that limits the accessibility of carbohydrates to the hydrolytic enzymes. Despite the progress made in developing innovative biomass delignification processes [3], some drawbacks still exist that need to be faced. Further efforts are therefore needed in order to identify biomass pretreatments that are able to break up the lignocellulosic structure, to decrease the cellulose crystallinity, and at the same time to provide a high hemicellulose recovery while limiting the formation of inhibitory compounds [4]. Moreover, most of the pretreatment processes requires large water, solvents or energy consumption and are typically implemented at large scale as first operation in the biorefinery sites. More versatile processes that might be locally applied for distributed production and collection of lignocellulosic feedstock are required in order to develop ‘intermediate’ carbon vectors in the form of stable and ready-to-use resources. To this aim, the investigation of mild thermochemical processes such as torrefaction can offer wide opportunities. Torrefaction is a mild thermo-chemical treatment where biomass is heated in an inert environment up to a temperature ranging between 200 and 300 °C. It is characterized by low particle heating rate (< 50 °C/min) and a relatively long reactor residence time (5 -120 min) [5]. Even though, so far, torrefaction has been mostly adopted as a biomass pretreatment technology for thermochemical conversion pathways (i.e. combustion, pyrolysis and gasification), there are evidence in the pertinent literature [6] that torrefied feedstocks can be enzymatically hydrolyzed for lignocellulosic bioethanol production. Brachi et al. (2017) [7] have also found that torrefaction promote the conversion of crystalline cellulose into an amorphous state, the latter being more susceptible to the enzymatic hydrolysis than the former. Among the other effects, torrefaction improves the grindability of fibrous materials [5], which may reduce the energy demand for grinding the feedstock before hydrolysis, and turned out to be a suitable pretreatment to improve the fuel properties of lignin residues resulting from enzymatic hydrolysis [8]. In the light of the abovementioned benefits, the potential of combining biomass torrefaction with enzymatic hydrolysis for lignocellulosic butanol and isopropanol production has been preliminary investigated in the present paper by using coffee silverskin as a feedstock. In more details, thermogravimetric runs and lab-scale fixed bed torrefaction tests have been carried out to identify the process temperature, which allows minimizing the content of lignin in the torrefied solid, while preserving the original amount of cellulose and hemicellulose. The basic idea is to exploit

the different thermal stability and reactivity that hemicellulose, cellulose and lignin exhibit because of their different composition and structure.

Experimental

Coffee silverskin (CS) residues used in this research were kindly provided by Illy S.p.A.. Batch torrefaction tests were performed at four different temperatures (i.e., 160, 180, 200 and 220 °C) by keeping the reaction time constant at 60 min. Nitrogen was used as the purge gas at a flow rate of 200 NL/h. In a typical experimental run, the reactor was loaded with about 6 g of CS particles (about 8%wt. moisture content) in the size range 1–2.8 mm, which were uniformly mixed with about 160 g of silica sand in the size range 3–4 mm to ensure a better temperature control throughout the packed bed and prevent the occurrence of localized hotspots. More detailed information about the experimental apparatus and the procedures adopted for torrefaction tests can be found elsewhere [5, 7]. The analysis of permanent gases evolved during the treatment of CS was performed in real time using a portable emission analyzer that allows monitoring the evolution of the main components of the ‘torgas’ (i.e., CO and CO₂) [5]. The analysis of liquid products, which were quantitatively recovered from the impinge bottles by washing them with acetone, was performed off-line using a GC-MS system (Agilent HP6890/HP5975) equipped with a flame ionization detector (FID). The proximate analysis of raw and torrefied biomass samples was performed by using a TGA 701 LECO thermogravimetric analyzer by following the ASTM D5142. The elemental composition (CHN) of samples was determined by using a CHN 2000 LECO analyzer according to the ASTM D5373 standard method. The oxygen content was estimated by difference. All the analyses were performed in duplicate at least. The higher heating value (HHV, MJ/kg, dry basis) was measured by using a Parr 6200 Isoperibol Calorimeter. The thermal decomposition behavior of CS was investigated using a TA Instruments analyzer Q600 SDT. In more details, a dynamic run at a heating rate of 5 °C/min was carried out over the temperature range from ambient to 800 °C. Nitrogen was used as the purge gas at a flow rate of 200 mL/min. Low sample mass (about 10 mg) and small particle size (0–500 µm) were selected in order to reduce the effect of interparticle mass and heat transport limitations during analyses. The biomass was characterized in terms of glucan, xylan, arabinan, and lignin composition according to the standard National Renewable Energy Laboratory (NREL) protocols [9].

Result and discussion

Fig.1a shows TG and DTG curves of raw CS as recorded under nitrogen atmosphere at 5 °C/min heating rate. Data show that the onset decomposition temperature of CS, which is dictated by the thermal stability of its hemicellulose component, is around 200 °C. Accordingly, since the basic idea behind this work is to exploit the different thermal stability of hemicellulose, cellulose and lignin in order to minimize the content of lignin in the torrefied solid, while preserving the original amount of cellulose and hemicellulose, torrefaction tests were performed varying the operative temperature in the range of 160–200 °C, whereas the reaction time was preliminary fixed at 60 min. Table 1 shows the mass yields of the main output products arising from CS torrefaction treatment. As expected, it was found that the yield in solid product (MY_S) decreases as temperature increased, whereas the yield of volatile products consisting of the condensable (MY_L) and the non-condensable (MY_G) fraction of the ‘torgas’ consequently increases. The elemental and proximate compositions of raw and torrefied CS are shown in Table 2 along with their content in glucan, xylan and lignin (Acid Insoluble Lignin and Acid Soluble Lignin). In line with previous research findings [5, 7], data show that the higher the torrefaction temperature, the lower the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) elemental ratios in torrefied solids and, consequently, the higher their calorific values with respect to that of the raw feedstock. Again, it was found that while the volatile matter (VM) decreased with an increase in the torrefaction temperature, the fixed carbon (FC) and ash contents increased.

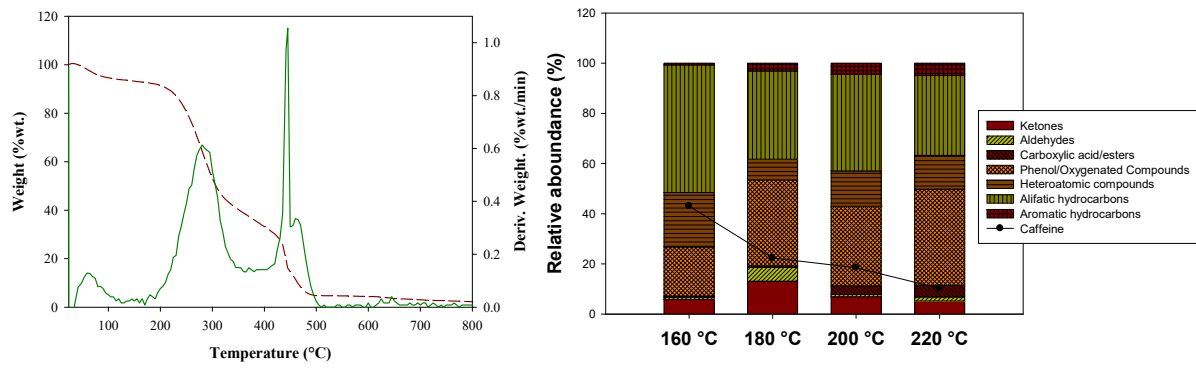


Fig. 1 a) TG and DTG curves of raw CS recorded under nitrogen atmosphere at 5 °C/min heating rate and b) chemical composition of the liquid products from torrefaction of CS.

It is worth noting that the decrease in the H/C and O/C elemental ratios makes the biomass more suitable for fuel application, particularly resulting in less smoke and water vapor formation, and reduced energy loss during subsequent combustion or gasification processes.

Table 1 Experimental conditions and torrefaction product yields

Test code	T (°C)	t (min)	Bed material	N ₂ (Nl/h)	MY _S	MY _L	MY _G [*]	MY _{CO} MY _{CO2}	
								(%wt., ar)	
CS160	160	60	Silica sand	200	84.20	2.79	13.01	0.20	1.94
CS180	180	60	Silica sand	200	74.27	2.24	23.50	0.67	3.11
CS200	200	60	Silica sand	200	58.24	6.23	35.53	0.85	4.97
CS220	220	60	Silica sand	200	48.06	12.33	39.61	1.01	4.95

* by difference

Table 2 shows data on structural carbohydrates and lignin (acid soluble and acid insoluble). The ASL is almost completely removed after torrefaction at 220°C (88% delignification) and it is halved (55% delignification) at 160°C. AIL is more recalcitrant to the thermal treatment and its reduction ranges from 6% (160°C) to 35% (220°C). Considering that the raw CS can not be hydrolyzed, as received, by commercial cellulase cocktails due to the hindrance effect of lignin, the such preliminary findings suggest that the production of hydrolytic sugars from torrefied CS by means of enzyme catalysis is worth being investigated further. However, following the requirement of maximum sugar recovery for the enzymatic hydrolysis, the torrefaction temperature should be kept at temperature levels as low as 160 °C because this condition results in a lower sugar loss (about 34%). In addition, the modifications of biomass structure that take place as a consequence of release of ‘torgas’, in particular the increase in the porosity [10], might result in a larger exposure of the cellulose and hemicellulose polymeric chains, which is beneficial for the hydrolysis step since the final solid might have larger substrate availability for the enzymes. Fig.1b shows the main components identified in the liquid products collected during the torrefaction treatment of CS, which were grouped into seven main categories based on their functionality. Data show that the condensable fraction of torgas evolved during CS torrefaction mostly consists of phenolic/oxygenated compounds, aliphatic hydrocarbons and heteroatomic species. It is worth noting that phenolic compounds, which derives from lignin and other plant components (mostly extractives), can pose significant inhibition on microbial conversion of lignocellulosic sugars during the eventual fermentation step [11]. This means that, their removal in the form of condensable compounds during torrefaction pretreatment may be beneficial for enzymatic hydrolysis of CS. Results also highlighted that, among the detected heteroatomic compounds, those with nitrogen heteroatom(s) only were the most abundant ones; in particular, caffeine (C₈H₁₀N₄O₂), was the nitrogenous organic compound present in larger amounts (up to 43%wt. in

the liquid product from torrefaction test at 160 °C, see Fig.1b). This finding suggests torrefaction as a potential technique to extract bioactive compounds (i.e., phenolic compounds and caffeine) from coffee silverskin [12]; the quantitative assessment of the condensable species evolved during the torrefaction treatment of CS under different operating conditions (i.e., temperature and time) deserves, therefore, further evaluation.

Table 2 Chemical composition and calorific values of torrefied coffee silver skin.

Test code	VM	FC	Ash	N	H/C	O/C	HHV	Glucan	Xylan	Arab	AIL	ASL
	(%wt., dry basis)				(-)		(MJ/kg, db)					
CSraw	78.0	17.1	4.9	2.8	0.14	0.80	19.8	17.5	9.6	2.5	29.9	4.1
CS160	73.3	19.2	7.5	2.9	0.12	0.59	20.7	16.5	6.8	n.d.	33.3	2.2
CS180	70.8	19.6	9.6	2.9	0.11	0.53	21.7	13.5	5.7	n.d.	35.5	2.1
CS200	65.9	26.2	7.9	3.2	0.10	0.48	23.6	8.12	2.7	n.d.	38.2	1.6
CS220	59.7	29.8	10.5	3.3	0.09	0.33	25.7	3.1	0.8	n.d.	39.9	1.1

VM= volatile matter; FC= fixed carbon; Rec.= recovery; AIL= acid insoluble lignin; ASL= acid soluble lignin

References

- [1] Pfromm, P.H., Amanor-Boadu, V., Nelson, R., Vadlani, P., Madl, R., 2010. Bio-butanol vs. bio-ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or *Clostridium acetobutylicum*. *Biomass. Bioenergy* 34, 515-524.
- [2] Raganati, F., Procentese, A., Olivieri, G., Russo, M.E., Gotz, P., Salatino, P., Marzocchella, A., 2016. Butanol production by *Clostridium acetobutylicum* in a series of packed bed bio-film reactors. *Chem. Eng. Sci.* 152, 678-688.
- [3] Procentese, A., Raganati, F., Olivieri, G., Russo, M.E., Rehmann, L., Marzocchella, A., 2017. Low-energy biomass pretreatment with deep eutectic solvents for bio-butanol production. *Bioresour. Technol.* 243, 464-473.
- [4] Akién, G., Qi, L., Horvath, I.T., 2010. Conversion of Carbohydrates to liquid fuels, in: Crocker, M. (Ed.), *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*. Royal Society of Chemistry, Cambridge, UK, pp. 32-373.
- [5] Brachi, P., 2016. "Fluidized bed torrefaction of agro-industrial residues: the case study of residues from Campania region, Italy". Ph.D. Thesis. ISBN 8878970735.
- [6] Chiaramonti, D., Rizzo A.M., Prussi, M., Tedeschi, S., Zimbardi, F., Braccio, G., Viola, E., Taddei Pardelli, P., 2011. 2nd generation lignocellulosic bioethanol: is torrefaction a possible approach to biomass pretreatment?. *Biomass Conv. Bioref.* 1, 9-15.
- [7] Brachi, P., Riianova, E., Miccio, M., Miccio, F., Ruoppolo, G., Chirone, R., 2017. Valorization of Sugar Beet Pulp via Torrefaction with a Focus on the Effect of the Preliminary Extraction of Pectins. *Energy Fuels* 31, 9595–9604.
- [8] Tregambi, C. Montagnaro, F., Salatino, P., Solimene, R., 2018. Torrefaction of a lignin-rich residue in a solar fluidized bed reactor. *Proceeding of Joint Meeting of the German and Italian Sections of the Combustion Institute*, Sorrento, Italy, 2018.
- [9] Sluiter, A., Hames, B., Ruiz, R., Scarlata, C. Sluiter, J., Templeton, D. Crocker, D., 2011. Determination of structural carbohydrates and lignin in biomass. Golden (USA): National Renewable Energy Laboratory (NREL). Report No.: NREL/TP-510-42618. Contract No.: DE-AC36-08-GO28308
- [10] Raut, M.K., Basu, P., Acharya, B., 2016. The effect of torrefaction pre-treatment on the gasification of biomass. *International Journal of Renewable Energy and Biofuels*, 2016, 1-13.
- [11] Tejirian, A., Xu, F. 2011. Inhibition of enzymatic cellulolysis by phenolic compounds. *Enzyme Microb. Technol.* 48, 239-247.
- [12] Ballesteros, L.F., Teixeira, J.A., Mussatto, S.I. 2014. Selection of the Solvent and Extraction Conditions for Maximum Recovery of Antioxidant Phenolic Compounds from Coffee Silverskin. *Food Bioprocess. Tech.* 7, 1322-1332.