Cellulose
DOI 10.1007/s10570-014-0484-z

ORIGINAL PAPER

Catalytic and catalytic free process for cellulose conversion: fast pyrolysis and microwave induced pyrolysis studies

María Luz Nieva · María Alicia Volpe · Elizabeth Laura Moyano

Received: 15 March 2014 / Accepted: 20 October 2014
© Springer Science+Business Media Dordrecht 2014

Abstract The catalytic and non-catalytic pyrolysis of microcrystalline cellulose and phosphoric acid pre-treated cellulose was investigated. The thermal processes were carried out applying two different methodologies: conventional fast pyrolysis and microwave-induced pyrolysis. For the catalytic experiments different catalysts were evaluated: CeO_2, Nb_2O_5, SiO_2, high surface area SiO_2, Si-MCM-48 and Al-Fe-MCM-48. In all cases the liquid fraction was evaluated by quantifying the yields of anhydrosugars (mainly levoglucosan, levoglucosenone and 1,4:3,6-dianhydro-α-D-glucopyranose) and aromatic hydrocarbons. In the reaction of microcrystalline cellulose levoglucosan was the main product, while levoglucosenone was predominant in the pyrolysis of phosphoric acid pre-treated cellulose. Catalysts improved the fraction of bio-oil and the product distribution depended on the nature of catalytic materials as well as the starting cellulose. On the other hand, the microwave induced pyrolysis favored the formation of char at expenses of liquid fraction. In this case levoglucosenone and other anhydrosugars in conjunction with furan compounds were the main products.

Keywords Cellulose · Pyrolysis · Catalysis · Microwave · Anhydrosugars

M. L. Nieva · E. L. Moyano (✉)
INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5016 Córdoba, Argentina
e-mail: lauramoy@fcq.unc.edu.ar

M. L. Nieva
e-mail: mnieva@plapiqui.edu.ar

M. L. Nieva · M. A. Volpe
Planta Piloto de Ingeniería Química, PLAPIQUI (UNS - CONICET), Cno. La Carrindanga Km. 7, 8000 Bahía Blanca, Argentina
e-mail: mvolpe@plapiqui.edu.ar

Introduction

Biomass, a renewable source for carbon based liquid fuels, has a potential to alleviate the dependency on fossil fuels and related environmental problems. One of the ways for upgrading biomass is the fast pyrolysis, which today is mainly carried out for obtaining bio-oil, employing short residence time (<2 s) and temperatures in the range of 400–500 °C. The bio-oil is a complex mixture of water, organic acids, aldehydes, ketones, alcohols, sugars, furans, phenols, among others. Due to the oxygen content of this liquid it cannot be directly employed as fuel requiring quality improvement (Czernik and Bridgwater 2004).

Alternatively, bio-oils containing valuable chemicals in significant concentrations may have also a potential use as a chemical feedstock (Bridgwater and Grassi 1991). However, these products are produced with a low yield and their separation from the liquid phase usually is extremely difficult. Chemicals include

Published online: 05 November 2014

anhydrosugars and their derivatives, namely levoglucosan (LG), levoglucosenone (LGO), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP), (1S,5R)-5-hydroxy-3,7-dioxabicyclo[3.2.1]octan-4-one (LAC), 2-furfural, 5-hydroxymethyl-2-furfural, among others.

Lignocellulosic biomass consists of three major components: cellulose, hemi-cellulose, and lignin. Cellulose and hemicelluloses are the carbohydrate polymers, and lignin is a cross-linked macromolecule. When biomass particles are exposed to high temperatures, different processes, such as de-polymerization of these polymers or fragmentations of macromolecules, condensation, and decomposition of monomers, proceed sequentially and/or in parallel, producing a complex mixture of volatiles, liquid products, and char residue (Vinu and Broadbelt 2012; Antal 1982). In the context of simplicity, the pyrolysis of cellulose, as a representative component of the biomass has been studied. However, despite their simple chemical structure, successful conversion of cellulose into specific substances used as chemical feedstock appears complicated. Two main competitive pathways are involved during cellulose pyrolysis: one which leads to the formation of LG as a relatively stable product and the second which yields glycolaldehyde and formaldehyde (Antal and Varhegyi 1995). The use of additives modifies the product distribution and composition of the bio-oils derived from cellulosic sources. Pretreatment is an important tool for practical cellulose conversion processes promoting the dehydration of the biopolymer and the formation of anhydrosugars and furans (Mosier et al. 2005). Thus, the use of acids (H_2SO_4 and H_3PO_4) decreases LG yields promoting the formation of LGO (Dobele et al. 1999, 2003) whilst the alkalis ($Ca(OH)_2$ and NH_4OH) seem to increase LG yield (Shaik et al. 2013).

In addition, plenty of different solid catalysts were used to perform catalytic pyrolysis of cellulose for chemicals production, using moderate temperatures and reducing the unwanted properties of the bioliquid (polymerization, high viscosity, oxygen content, among others). Many studies have been carried out applying different catalysts as zeolites (Fabbri et al. 2007), silica (Choi et al. 2011), metal oxides (Fabbri et al. 2007; Lu et al. 2009), clays (Rutkowski 2012), and mesoporous solids (Torri et al. 2009), just to mention a few examples. Bulky organic molecules are formed during pyrolysis of biomass interacting with the accessible catalyst surface. Over this surface, and more specifically over acid sites, the molecules undergo scission of different types of bonds. Thus, textural properties (specific surface area, size, geometry and volume of pore) and acidity (strength and concentration of acid sites) are important parameters of the catalysts which play a paramount role in these reactions.

Thermochemical conversion of cellulosic materials can also be achieved by microwave heating (Motasemi and Afzal 2013; Shra'ah and Helleur 2014; Yin 2012). This technique not only reduces the energy consumption and processing time, but also enables the employment of novel chemistry tools. In conventional thermal heating, the energy is transferred from source to the center of material via radiation, convection, and conduction, while in microwave or dielectric heating the electromagnetic energy is converted to thermal energy inside the sample. The microwave-assisted reactions can be completed more efficiently in comparison with other thermal methods due to efficient heat transfer profiles. For this reason, microwave heating appears as one of the promising techniques for carrying out the biomass pyrolysis process, accelerating the chemical reactions and reducing the processing costs.

In the present work the catalytic and catalytic free pyrolysis of microcrystalline cellulose and phosphoric acid pre-treated cellulose were carried out. Pyrolysis experiments were performed applying two different methodologies, one dynamic (fast pyrolysis) and other static (microwave-induced pyrolysis). For catalytic experiments a series of heterogeneous catalysis displaying different structural and physicochemical properties were evaluated: CeO_2, Nb_2O_5, SiO_2 (low and high surface area), siliceous MCM-48 and Al-Fe-MCM-48. The aim of this study was to establish the differences between all pyrolytic systems for treatment of two cellulosic materials, in the context of employing the resulting bio-oil as a potential source of renewable fuel and/or a chemical feedstock.

Materials and methods

Cellulose samples

Commercial microcrystalline cellulose from Biopack was selected for the pyrolysis study. The cellulose was pre-treated by impregnation with phosphoric acid

(Anedra, 85 % w/w) solutions. In this procedure 1.00 g of cellulose and 5 ml of 5 % (w/w) phosphoric acid aqueous solution were introduced in a round-bottom flask and kept at 70–80 °C under magnetic stirring. Following 2 h, the mixture was filtered under vacuum and the solid was dried at 40 °C under vacuum overnight.

In the microwave-assisted impregnations, the mixture of cellulose (1.00 g) and phosphoric acid solution (5 ml, 85 % w/w) was irradiated for 5 min at 70 °C and 300 W using a CEM-Discovery Labmate equipment. Then, the mixture was filtered under vacuum and the solid was dried indistinctly at 40 °C under vacuum overnight or at 100 °C at atmospheric pressure by 2–3 h. The type of drying did not affect the quality of the material.

Cellulose materials were characterized by two X-ray diffraction (XRD) equipments: a Philips PW1710 BASED instrument operating at 45 kV and 30 mA, fitted with a graphite monochromator in order to get Cu Kα1 radiation ($\lambda = 1.5406$ Å) and a Panalytical X'Pert Pro (40 mV, 40 mA), Cu Kα ($\lambda = 1.5418$ Å).

Crystallinity index of microcrystalline and pretreated cellulose was calculated based on the data of X-ray diffractometry (Ioelovich et al. 1989). Besides, these materials were studied by Scanning Electron Microscopy (SEM) on a Jeol 100 CX2 (Tokyo, Japan) apparatus.

Catalysts preparation and characterization

Four commercial catalysts were employed for carrying out the pyrolysis: CeO_2 (from Rhöne Poulenc, 240 m^2/g), SiO_2 (Davison, 210 m^2/g), high surface area SiO_2 (Aldrich, 810 m^2/g) and Nb_2O_5 (CBMM, Brazil, 150 m^2/g). Besides two mesoporous catalysts, siliceous MCM-48 and Al-Fe-MCM-48 were prepared. The former sample was obtained by a classical hydrothermal synthesis following the procedures reported elsewhere (Xu et al. 1998; Bore et al. 2006). Briefly, cetyl trimethyl ammonium bromide was employed as the surfactant, while sodium silicate was the silica source. The Al-Fe-MCM-48 sample was obtained by adding Al and Fe nitrates to the precursor solution in order to obtain a Si/Me (Me: Fe or Al) ratio of 60. All catalysts employed in this work were characterized in order to determined several physicochemical properties: crystallinity, specific surface area, pore volume and the acidic properties (number of acid sites per m^2 and strength of the acid sites).

X-ray diffraction patterns of catalysts before and after the pyrolysis experiments were recorded in a Siemens D5000 diffractometer using a Cu Kα radiation and 2 sets of 1° Soller slits and a graphite monochromator. The data were collected in the 2θ range: 15.800°–140.000°, the scanning step was 0.025°, 4,969 points were measured with a counting time of 20 s per point.

The specific surface area of the catalysts was determined by adsorption–desorption of N_2 at 77 K employing a Nova 1200e Quantachrome equipment by using the BET equation for surface area. The diameter of the porous as well as the pore volume was also measured following the BJH approximation. Samples were evacuated at 393 K for 4 h before the measure.

The acidity of the catalysts was studied by temperature programmed desorption of ammonia (NH_3-TPD) which is a traditional method for determining the surface acidity in heterogeneous catalysts. The amount of NH3 adsorbed per gram of catalyst was determined as it was early described (Tonetto et al. 2004; Garcia et al. 2005). Besides, a titration method was employed for determining the concentration of acid sites, as well as the corresponding strength (Cid and Pecchi 1985; Covarrubias et al. 2009). This procedure was previously employed for some of us for studying the strength and the concentration of heterogeneous ceria catalysts (Diez et al. 2014). Approximately 100 mg of catalyst was dispersed in 100 ml of acetonitrile, then the mixture was stirred for 1 h and afterwards it was titrated with a 0.10 M solution of *N*-butylamine employing an AT500N Automatic Potentiometric Titrator. The total surface acidity was evaluated from the amount of base added to reach the *plateau* in the titration curve, while the first point of the titration (E0, mV) was employed for analyzing the acid strength.

Pyrolysis experiments

The fast pyrolysis reactions were conducted in a tubular reactor under inert atmosphere. The quartz reactor with a length of 25.00 cm and an inner diameter of 2.50 cm was heated externally by using a tube furnace with a temperature-controller device. The reactor was connected to a high vacuum pump where pressures were in the range of 0.01–0.05 Torr.

Granulated cellulose samples (1.00 g) were placed in a sliding ceramic boat, which was fed into the pyrolysis furnace when temperature (250–400 °C) and vacuum conditions were reached. Thus, the sample was subjected to pyrolysis conditions for 20 min and contact times were very short (<0.1 s). Oxygen-free dry nitrogen was used as inert carrier gas to improve the transportation of products to the condensation region and nitrogen flow rate were 0.1 mL/s[1]. Liquid products were trapped at liquid air temperature immediately they escape the hot zone. The pyrolysate was extracted with acetone and subjected to different analyses or separation techniques. After evaporation of organic solvent, the liquid phase consisting of oil was weighed. The solid char was removed from the ceramic boat and also weighed and then the gas yield was calculated by difference. All yields are expressed as the average of at least three experiments to confirm the reproducibility of the reported results.

In the catalytic pyrolysis, cellulose blends with 10 % (w/w) catalyst addition were pressed and then fractured to 10–20 Mesh size particles.

In the microwave-induced experiments, 0.20 g of cellulose (microcrystalline or pre-treated) were irradiated at different times (2–15 min), temperatures (200–300 °C) and power (150–300 W) in a closed-vessel quartz reactor. In the catalyzed reactions, cellulose (0.20 g) and catalysts (10 % w/w) were exhaustively mixed in a mortar prior to the irradiation. After finishing the reaction, the mixture was treated with acetone and the solid was filtered and dried to calculate the yields of products. The acetone solution was analyzed by gas chromatography/mass spectrometry (GC/MS).

For the isolation of LGO and its subsequent identification by NMR (^{1}H and ^{13}C) and IR analyses, the oil mixture obtained in the pyrolysis of pre-treated cellulose was purified using a column chromatographic on silica gel and a mixture of chloroform: ethyl acetate (80:20 and 70:30) as eluent.

Gas chromatography/mass spectrometry analyses were performed in a Shimadzu GC–MS-QP 5050 spectrometer. The injector temperature was kept at 300 °C and the separation was performed using a VF-5 ms capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium was used as carrier gas with a constant flow rate of 0.5–1.0 μl/min. The oven temperature was programmed from 80 °C (3 min) to 280 °C (15 min) with the heating rate of 10 °C/min. The temperature of the GC/MS interface was held at 280 °C, and the mass spectrometer was operated at 70 eV. The mass spectra were obtained from 40 to 400 m/z with the scan rate of 500 amu/s. The identification of chromatographic peaks was achieved according to the NIST MS library.

^{1}H and ^{13}C spectra were recorded in acetone-d_6 with a Bruker Avance II 400 MHz spectrometer (BBI probe, z gradient) (^{1}H at 400.16 MHz and ^{13}C at 100.56 MHz). Chemical shifts are reported in parts per million downfield from TMS. The spectra were measured at 22 °C. Infrared solid spectra were recorded with an FTIR Bruker IFS 28v spectrometer, with a resolution of 2 cm^{-1} in the range from 4,000 to 400 cm^{-1} by using KBr disks.

Results and discussion

Characterization of cellulose materials

Microcrystalline cellulose (from now on "MCC") and phosphoric acid-treated cellulose (from now on "TC") samples were analyzed by XRD diffraction. The diffraction peaks of cellulose crystals were observed in both cases (Fig. 1). From the width of these peaks the crystalline index of the samples was determined, giving rise to a value of 81 % and of 69 % for MCC and for TC, respectively. Thus, the acid treatment was effective for reducing the number of ordered micro-regions of the macromolecule increasing the relative content of amorphous regions, which is in agreement with previous studies regarding structural changes of cellulose after impregnation with phosphoric acid (Dobele et al. 2001; Zhang et al. 2009).

The morphologic modification of the cellulose after acid treatment can also be examined by SEM analysis (Fig. 2). Thus, cellulose ribbons are clearly observed for the non-treated sample (Fig. 2a) together with minor amorphous regions. On the other hand, TC consists of a very large amount of cellulose agglomerates where fibbers are distinctly reduced in length compared with MCC (Fig. 2b). A closer look at the macrofibril surface, at larger magnification, showed many terraces, steps and kinks. This change can be attributed to the surface dehydration of the cellulose catalyzed by the acid (Zhao et al. 2007).

On the other hand it is known that microwave drying is a rapid and high-effect method to decrease the moisture content of biomass materials to produce

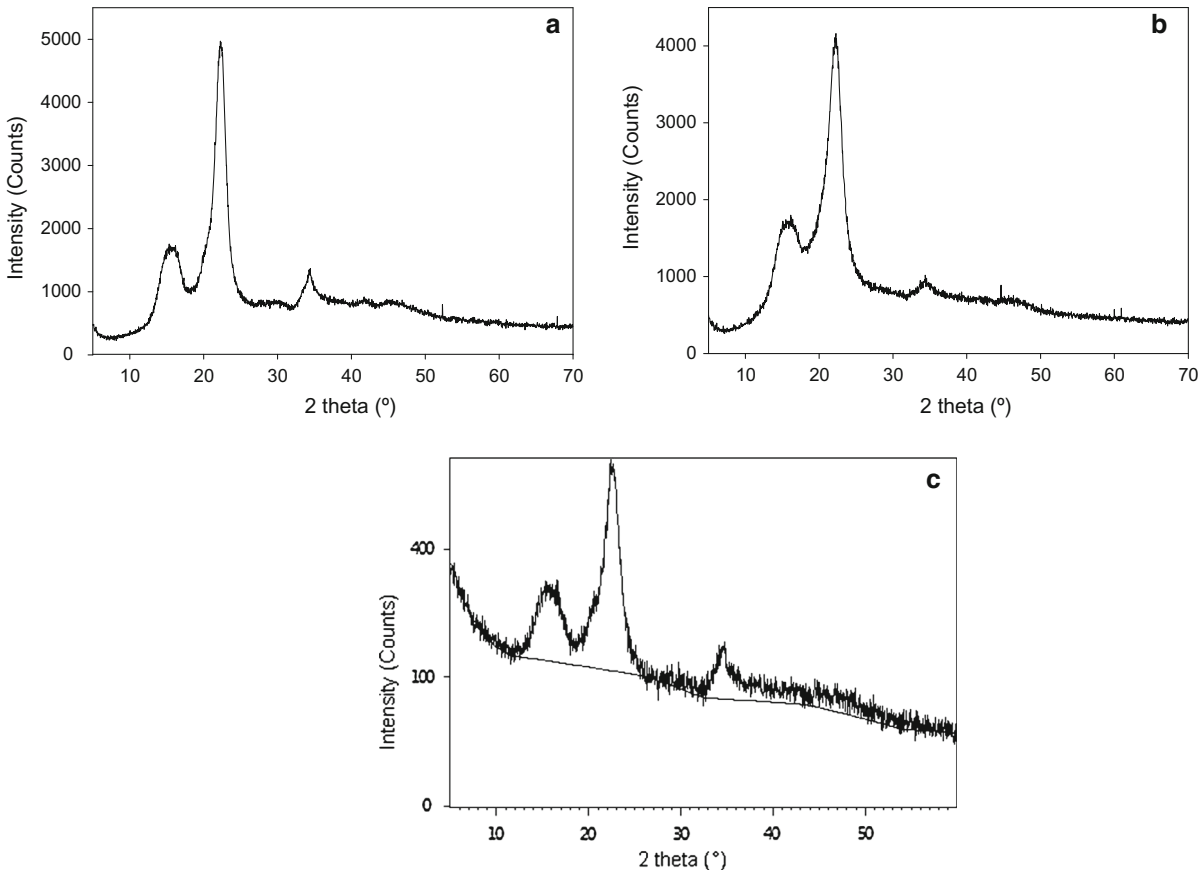

Fig. 1 XRD patterns of cellulose samples: **a** microcrystalline cellulose (MCC), **b** acid treated cellulose (TC) and **c** microwave acid treated cellulose (MTC)

higher quantity and better quality bio-oil during the fast pyrolysis process (Wang et al. 2008). Additionally the use of microwave technology can successfully facilitate acid hydrolysis of cellulose allowing high yields of glucose in short reaction times (Orozco et al. 2007). Thus, to study the influence of microwave irradiation in the impregnation process, a mixture of cellulose and phosphoric acid solution was irradiated at 70 °C and 300 W during 5 min. SEM micrographs showed a different morphology for microwave irradiated cellulose respect to MCC (Fig. 3). The agglomeration of macrofibrils was increased, even though the length of fibrils can be difficult to measure, they are clearly shortened. However, the formation of agglomerates was less than in cellulose treated with phosphoric acid using the conventional heating during the impregnation.

Characterization of heterogeneous catalysts

For all catalysts, BET specific surface areas and specific pore volume derived from nitrogen adsorption–desorption measurements are summarized in Table 1 along with the acidity determinations. The BET area of the mesoporous solids showed large values as could be expected for these materials. Volume pore values were also significant for mesoporous solids. In addition it was determined that the pore diameter of Al and Fe substituted MCM-48 was 4.1 nm, while the one for pure MCM-48 was 3.8 nm. This change revealed how effectively was the incorporation of metal atoms into the framework. Similar observations on increments in pore diameter for metal substituted MCM-48 materials have also been reported (Kong et al. 2005; Jha et al. 2006). Nitrogen

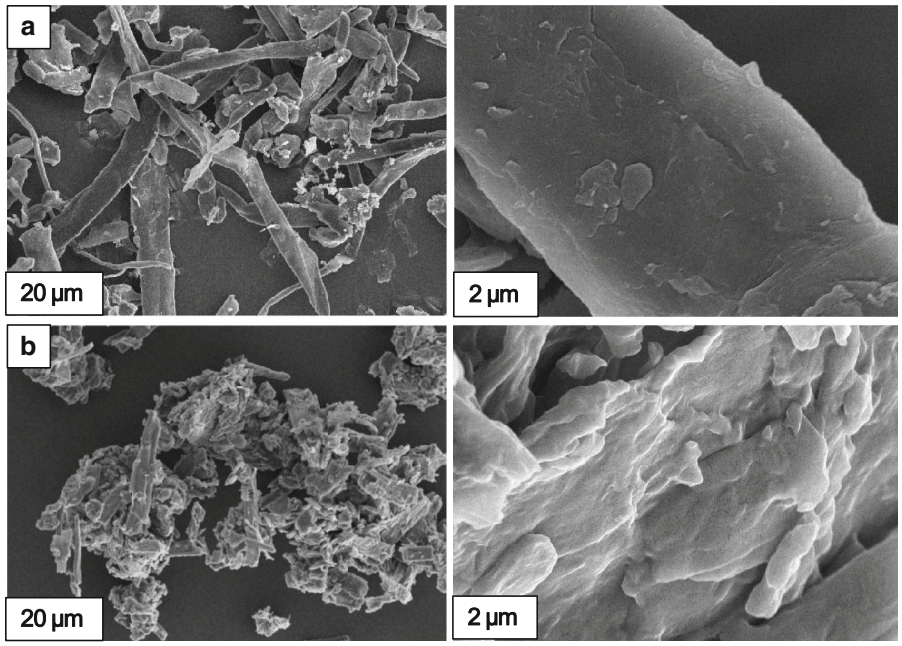

Fig. 2 SEM micrographs of cellulose samples at low and higher magnification: **a** MCC and **b** TC

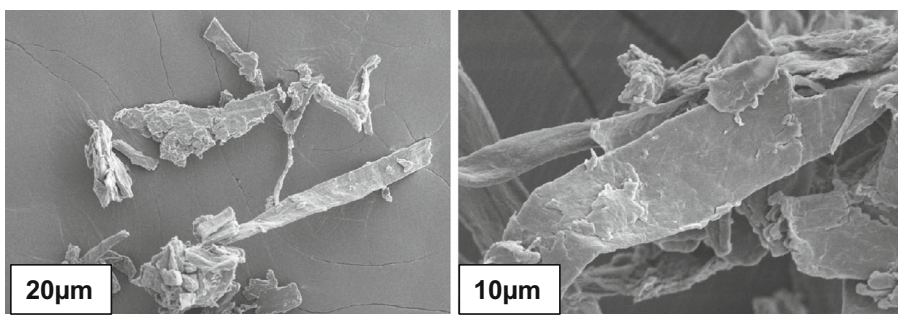

Fig. 3 SEM micrographs of cellulose after microwave acid treatment at low and higher magnification

adsorption isotherms of CeO_2, Nb_2O_5 and SiO_2 exhibited the type corresponding to microporous solids showed lower specific surface area and pore volume while SiO_2 with high surface area (from now on HAS-SiO_2) presented a similar behaviour to the mesoporous materials.

Concerning to the acidity, the concentration of acid sites as measured by NH_3-TPD is reported in Table 1. It can be determined that all catalysts show acidic surface sites, showing the following decreasing order of concentration of acid sites (as measured by ml of NH_3 adsorbed per g of catalysts): $Nb_2O_5 > CeO_2 >$ Al–Fe-MCM-48 > HSA-SiO_2 > MCM-48 > SiO_2. The same order of acidity was confirmed by the titration with *N*-butylamine (see Table 1), for which the concentration of acid sites was measured as miliequivalents (mEq) of base per gram of catalyst. The strength of the acid sites is also reported in Table 1. Regarding the mesoporous catalysts MCM-48 and Al-Fe-MCM-48, the data indicate that acidity is increased due to the incorporation of aluminium and iron ions into the MCM structure, both from the point of view of concentration and of the strength of the sites. The measurements indicated that SiO_2 should be considered to possess a low acidity, however, the high surface silica showed an increment of the acidity. These results also corroborated the high acidic properties of ceria and especially of niobia, respect to the other materials.

Table 1 Physicochemical properties of the catalysts

Catalysts	BET area (m^2/g)	Pore volume (cm^3/g)	Acidity determination		
			mL NH_3/g[a]	mEq base/g[b]	Acidic strength[b]
Nb_2O_5	143	0.06	9.1	1.20	s
CeO_2	240	0.10	5.0	0.72	s
SiO_2	310	0.05	0.7	n.d[c]	vw
HSA-SiO_2	810	0.4	3.3	0.51	w
Si-MCM-48	1,100	0.6	2.2	0.10	w
Al–FeMCM-48	1,250	0.9	3.8	0.41	vs

s strong acidity, *vs* very strong acidity, *w* weak acidity, *vw* very weak acidity

[a] Measured by TPD of adsorbed ammonia

[b] Measured by potentiometric titration with *N*-butylamine

[c] Non detected

Table 2 Experimental results of microcrystalline cellulose (MCC) and acid-treated cellulose (TC) fast pyrolysis

Cellulose	T (°C)	Yields of fractions (%)[a]			Products of liquid fraction (%)				
		Liquid	Solid	Gas	LGO	LG	AH	AS	Others[b]
MCC	250	3.0 ± 0.2	69 ± 4	28 ± 2	23	2	44	2	29
MCC	300	25 ± 2	23 ± 2	52 ± 4	7	48	2	30	13
MCC	350	38 ± 2	6.0 ± 0.4	56 ± 3	10	84	0	6	0
MCC	400	54 ± 4	5.0 ± 0.4	41 ± 3	1	80	0	2	17
MCC	500	59 ± 5	3.0 ± 0.3	39 ± 3	4	84	5	3	4
TC	250	5.0 ± 0.5	44 ± 4	52 ± 5	87	0	9	1	3
TC	300	7.0 ± 0.8	37 ± 4	56 ± 6	87	0	12	0	1
TC[c]	300	35 ± 2	22 ± 1	43 ± 3	62	0	29	5	4
TC	350	10 ± 1	40 ± 4	50 ± 6	50	0	2	48	0
TC	400	9 ± 1	36 ± 4	55 ± 6	31	15	4	49	1
TC	500	10 ± 1	25 ± 2	65 ± 7	3	9	60	19	9

LGO levoglucosenone, *LG* levoglucosan, *AH* aromatic hydrocarbons (ethylbenzene and xylenes), *AS* anhydrosugars (1,4:3,6-dianhydro-α-D-glucopyranose (DGP) and 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-4-one (LAC))

[a] Values expressed as average of 3–4 measurements with their analytical errors

[b] Mainly 5-methyl-furan-2-one, 5-methyl-2-furancarboxaldehyde, and 4-hydroxy-5,6-dihydropyran-2-one

[c] Cellulose impregnated with phosphoric acid using microwave heating

Fast pyrolysis of cellulose

Non-catalytic fast pyrolysis experiments of MCC and TC were carried out at different temperatures: 250, 300, 350, 400 and 500 °C, while catalytic pyrolysis were performed at 300 °C. For catalytic experiments CeO_2, Nb_2O_5, SiO_2, HSA-SiO_2, siliceous MCM-48 and Al-Fe-MCM-48 were used as solid and thermostable catalysts.

Non-catalytic pyrolysis experiments

An effective transformation of MCC began at temperatures higher than 200 °C and the liquid fraction increased with the increase of temperatures giving good yields at 400 °C (Table 2). The amount of bio-oil stayed almost the same at 500 °C from which it started to decline and gaseous products are predominant. By

contrary, the fraction of solid decreased with the temperature and only 3 % of char remained at 500 °C.

The impregnation of cellulose with phosphoric acid diminished considerably the formation of liquid products, giving acceptable yields only in the case of the microwave pretreated sample at 300 °C. This finding was in agreement with the morphologic changes of the cellulosic materials observed upon the acid treatment (Fig. 3), which showed a less degree of dehydration keeping mainly the fibrillar structure found in the MCC. It is known that microwave irradiation of different types of biomass increases the yield of bio-oil, while the yield of gas decreases. An explanation can be that larger surface area is developed by the material, and concomitantly the volatiles can easily leave the char layer minimizing the secondary reactions (Wang et al. 2008). It becomes clear that pyrolysis of TC produced high amounts of char and gas products at all evaluated temperatures (Table 2).

The liquid fraction was extensively analyzed by GC/MS technique, where the peak area percentage of the detected products depends on the response factor of the mass spectrometer detector, turning difficult the accurate quantification of products. Having that in mind, the peak area of an individual compound was considered to be directly proportional to the concentration of such compound in the liquid pyrolysate. Thus, the peak area percentage of a compound was used to compare the changing of its relative amount in the bio-oil at the experimental conditions studied.

According to the ion chromatograms, fast pyrolysis of MCC at temperatures higher than 300 °C gave high yields of LG, which was the main product (Dobele et al. 2001). The pyrolytic mechanism of cellulose degradation has been largely studied by several authors (Antal 1982; Pikorz et al. 1986; Shen and Gu 2009). It is proposed that decomposition of cellulose can be represented by two competitive reactions where one is the formation of anhydrocellulose and the other is the depolymerization to form LG, which can undergo dehydration and isomerization to form other anhydrosugars, including LGO and DGP (Oknishi et al. 1981). The thermal behavior of LG was verified when fast pyrolysis of pure LG was carried out at 250 °C and 0.05 Torr in our reaction system. Under these conditions, the composition of the pyrolysate was 29 % of LGO, 24 % of aromatics, 12 % of DGP and 36 % of un-reacted LG.

On the other hand, although LG can dehydrate to give LGO at low temperatures, the amount of LG in the pyrolysate at 250 °C was much reduced (only 2 %). Moreover, our pyrolysis study of LG corroborated that this compound was thermally stable, generating only 29 % of LGO during the pyrolysis. Therefore we may conclude that LGO, detected at low temperatures, was produced concurrently with LG, and did not emerge from transformation of this latter compound. The formation of LGO required the combined glycosidic bond cleavage and intramolecular dehydration reactions. According to previous studies, these two reactions could take place in different orders; resulting in the different LGO formation pathways (Oknishi et al. 1981). This fact could explain the considerable amounts of LGO at temperatures where LG formation was strongly not favored.

Apart from the anhydrosugars, other compounds were detected in the pyrolysis of MCC: aromatic hydrocarbon like xylenes and ethylbenzene, and different furan derivatives. It is well known that the formation of these products takes place through different reactions including fragmentations, rearrangements and aromatization (Paine et al. 2008; Li et al. 2013).

In the case of fast pyrolysis of TC, a different behavior was observed. LGO was the main product until 400 °C and LG was detected in few amounts at high temperatures. A similar behavior was previously observed in the thermal study of cellulosic materials impregnated with phosphoric acid indicating the effect of the acid treatment on the predominant formation of LGO (Dobele et al. 2001). Other anhydrosugars, especially the glucopyranose DGP, were also predominant in the reaction mixture up to temperatures of 500 °C and for higher temperatures aromatic hydrocarbons were the main products (Table 2). DGP is proposed to be an intermediate in the dehydration of LG to form LGO and its formation can be strongly affected by the reaction conditions (Shafizadeh et al. 1978; Rutkowski 2012).

Catalytic reactions

Taking into account the results obtained in the fast pyrolysis of MCC and TC, we decided to explore the influence of different heterogeneous catalysts in the transformation of cellulose. It is known that the

Table 3 Experimental results of catalytic fast pyrolysis of microcrystalline cellulose (MCC) and acid treated cellulose (TC) compared to non-catalytic pyrolysis

Cellulose	Catalyst	T (°C)	Yields of fractions (%)[a]			Products of liquid fraction (%)			
			Liquid	Solid	Gas	LGO	LG	AH	AS
MCC	–	300	25 ± 2	23 ± 2	52 ± 4	7	48	2	30
MCC	Nb_2O_5	300	45 ± 3	8.1 ± 0.5	47 ± 3	1	95	1	3
MCC	CeO_2	300	41 ± 3	8.0 ± 0.5	51 ± 3	6	75	2	16
MCC	SiO_2	300	44 ± 3	10.0 ± 0.6	46 ± 3	4	89	0	6
MCC	HSA-SiO_2	300	42 ± 3	12.0 ± 0.8	46 ± 3	1	81	3	15
MCC	AlFe-MCM-48	300	40 ± 3	10.0 ± 0.7	49 ± 3	2	90	2	5[b]
MCC	MCM-48	300	31 ± 2	18 ± 1	51 ± 3	16	29	2	53[b]
MCC	MCM-48	350	44 ± 3	15 ± 1	41 ± 2	0	57	2	41[b]
TC	–	300	7.0 ± 0.8	37 ± 4	56 ± 6	87	0	12	0
TC	Nb_2O_5	300	19 ± 1	36 ± 2	45 ± 2	37	30	3	30[c]
TC	CeO_2	300	10.0 ± 0.6	35 ± 2	55 ± 4	35	10	0	55[d]
TC	SiO_2	300	3.0 ± 0.2	39 ± 2	58 ± 4	46	0	1	54[e]
TC	HSA-SiO_2	300	20 ± 1	36 ± 2	44 ± 3	81	0	0	16[f]
TC	AlFe-MCM-48	300	12.0 ± 0.8	36 ± 2	52 ± 3	95	0	0	3
TC	MCM-48	300	16 ± 1	28 ± 2	56 ± 4	60	4	28	5
TC	MCM-48	350	10.0 ± 0.6	36 ± 2	55 ± 3	96	0	0	4

LGO levoglucosenone, *LG* levoglucosan, *AH* aromatic hydrocarbons (ethylbenzene and xylenes), *AS* anhydrosugars (1,4:3,6-dianhydro-α-D-glucopyranose (DGP) and 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC))

[a] Values expressed as average of 3–4 measurements with their analytical errors

[b] DGP was the only anhydrosugar detected

[c] 13 % of DGP and 17 % of LAC

[d] 21 % of DGP and 34 % of LAC

[e] 16 % of DGP and 38 % of LAC

[f] 7 % of DGP and 9 % of LAC

addition of a solid catalyst in the pyrolysis reactor allows in most cases the control over product distribution giving higher yields towards useful chemicals. For this study we selected six catalysts displaying different structural and acid properties: Nb_2O_5, CeO_2, SiO_2, HSA-SiO_2, pure siliceous MCM-48 and Al–Fe-MCM-48. The catalytic effect in the distribution of the liquid, solid and gas fractions as well as the bio-oil composition was investigated at 300 °C. This temperature was chosen because this value is substantially lower than temperature of non-catalytic pyrolysis of cellulose where formation of bio-oil was the greatest (Table 2). In addition, preliminary tests have shown that the chemical structure of all catalysts remained unaltered at 300 °C under the pyrolysis conditions.

Thus, the pyrolytic behaviour of MCC in the presence of catalysts changed substantially, in comparison with the un-catalysed cellulose at the same temperature. All catalysts promoted formation of liquid product (31–45 % yields) at the expense of the gas and solid fractions diminution (see Table 3). The catalytic effect of siliceous MCM-48 was less pronounced, for this reason, we decided to perform the pyrolysis at 350 °C and in this case yields of bio-oil were similar to those obtained for other catalysts at 300 °C. According to these evidences, all catalysts increased the production of bio-liquid at a lower temperature than required for similar conversion in the un-catalysed pyrolysis.

Since the catalysts under study show quite different acid properties, it could be postulated that the acidity of the samples do not play a crucial role in the observed increment in the liquid formation. It is more likely that this enhanced production would be linked to the presence of a heterogeneous surface in contact with the cellulose. May be there were not any

specifically interaction between the active sites of the different types of catalysts and pure cellulose. Thus, the increment of liquid fraction could be attributed to a better heat transfer from the catalyst surface to the biopolymer helping its degradation.

When the catalytic experiments were carried out using cellulose impregnated with phosphoric acid the quantity of liquid and solid fractions increased slightly. In comparison with catalysis free-reactions of TC, the presence of Nb_2O_5 and HSA-SiO_2 improved the bio-oil formation. In this case, the partially hydrolyzed cellulose interacted in the best way with niobia than ceria in the case of metal oxides. The higher performance of niobia by comparison with ceria would be due to the higher concentration of acid sites in the former than in the latter (see Table 1). For pure siliceous catalysts the catalytic effect was better for HSA-SiO_2 than SiO_2 and Si-MCM-48. Once again the acid character of the samples would be responsible for the observed differences. Thus, according to these facts, the acidity of the catalysts played an important role if we compare the behavior of materials having similar chemical features. In the case of Al-Fe-MCM-48-catalysed reactions, the formation of bio-oil was not significantly improved despite the increment of acid sites given by the incorporation of Al and Fe into the mesoporous framework. May be the extended surface area developed by this catalyst favored the presence of gaseous products.

These results underline the multitude of factors related to the starting material (crystallinity, impregnation type) as well as the catalyst (specific surface area, porosity, acid properties) affecting the production of the different fractions in the pyrolysis of cellulose.

About the composition of the bio-oil, a relatively high concentration of LG was detected for all catalytic reactions of MCC. Considering that the amount of the liquid fraction was highly increased, the yield of LG from the catalytic pyrolysis was notably increased by comparison with un-catalysed pyrolysis.

The Si-MCM-48/cellulose system displayed a different behavior in comparison with the other catalytic reactions. Thus, at 300 °C a poor yield of LG was obtained (29 %) but increased to 57 % when pyrolysis was conducted at 350 °C. In addition, a higher formation of DGP accompanied by an incremented production of LGO was found at 300 °C. These findings may indicate that structural and/or physico-chemical features of this material favored the dehydration of LG particularly to DGP and, to a lesser extent, to LGO. Such particular features would be the low concentration and strength of acid sites of the sample in combination with the large surface area.

A complex behavior was obtained when TC was evaluated with the different catalysts. Yields of LGO were much higher in the MCM-48 and HSA-SiO_2-catalysed reactions. By contrary, ceria, niobia and silica gave rise to pyrolytic oil enriched in DGP and LAC and depleted in LGO. The above results clearly indicated that the transformations of LG to more dehydrated/deoxygenated products depended on the type of catalysts. Thus, high surface area materials favored the transformation of LG to LGO, while oxides with low surface areas promoted the formation of DGP and LAC as the most important components of bio-oil. LAC is an important chiral anhydrosugar firstly identified by Furneaux et al. who also proposed its formation pathway from 1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose (APP) as intermediate (Furneaux et al. 1988). It could be concluded that the acid properties of the catalysts would not have a key effect in these transformations.

All the results obtained indicated that the composition of anhydrosugars in the pyrolysate was strongly influenced by the nature of starting cellulose as well as the type of catalyst. Thus, for pyrolysis of pure cellulose the application of catalyst improved the production of LG in comparison with non-catalytic reactions. In the pyrolysis of impregnated cellulose only mesoporous catalysts improved the yields of LGO, which was predominant in the un-catalysed reactions. The rest of catalytic materials favored the production of other important anhydrosugars as LAC and DGP. The behavior of the catalysts can be attributed to different effects and further examinations of the phenomena are necessary for better understanding of the overall catalytic process.

The regeneration and recyclability of the catalyst are important features to be evaluated taking into account the relative large quantity employed in the catalytic reactions. In order to study the reutilization of SiO_2 and CeO_2, the recycling tests were performed. Thus, the solid obtained in the first catalytic pyrolysis (SiO_2-I and CeO_2-I) was activated by calcination at 500 °C for 5 h, mixed with fresh cellulose and submitted to pyrolysis again. For ceria, the solid obtained in this second experiment (CeO_2-II) was also calcinated and then mixed with fresh cellulose for a

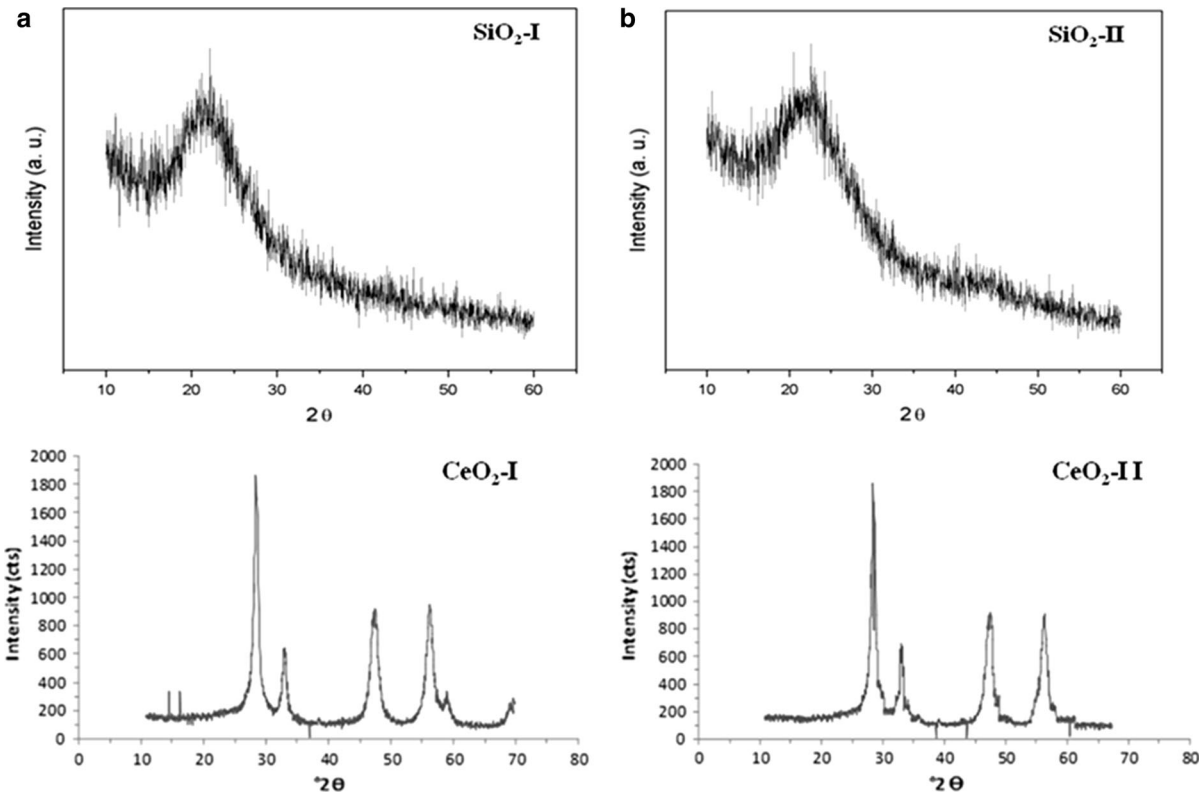

Fig. 4 XRD patterns of calcinated SiO_2 and CeO_2 after: **a** one pyrolysis and regeneration and **b** two pyrolysis and regenerations

Table 4 Distribution products in the catalytic fast pyrolysis of MCC using fresh and regenerated catalysts

Catalyst	T (°C)	Yields of fractions (%)[a]			Products of liquid fraction (%)			
		Liquid	Solid	Gas	LGO	LG	AH	AS
SiO_2[b]	300	44 ± 3	10.0 ± 0.7	46 ± 3	4	89	0	6
SiO_2-I[c]	300	38 ± 2	10.0 ± 0.7	52 ± 3	9	67	17	7
CeO_2[b]	300	41 ± 2	8.0 ± 0.5	51 ± 3	6	75	2	16
CeO_2-I[c]	300	38 ± 2	20 ± 2	42 ± 2	2	80	1	16
CeO_2-II[d]	300	14.0 ± 0.9	26 ± 2	60 ± 5	0	16	77	3

LGO levoglucosenone, *LG* levoglucosan, *AH* aromatic hydrocarbons (ethylbenzene and xylenes), *AS* anhydrosugars (DGP and LAC)

[a] Values expressed as average of 3-4 measurements with their analytical errors

[b] Fresh catalyst

[c] Catalyst after one calcination

[d] Catalyst after two calcinations

third pyrolytic experiment. After the calcinations, XRD analysis of silica and ceria showed than these solids kept the crystal structure (Fig. 4). However, analysis of products indicated that the catalytic behavior of these materials changed after the first pyrolysis. Thus, the reutilization of SiO_2 modified the composition of the liquid pyrolysate promoting the formation of aromatic hydrocarbons at the expense of LG (Table 4) although the quantity of liquid, solid and gas fractions remained the same. For ceria-catalysed reactions, after the first calcination, the formation of bio-oil as well as the yield of LG was not much

Table 5 Distribution of products in the microwave-induced pyrolysis of cellulose

Type of cellulose	Catalyst[a]	T (°C)/power (W)[b]	t (min)[c]	Yields of fractions (%)[d]			Products of liquid fraction (%)			
				Liquid	Solid	Gas	LGO	AS	Fur[e]	AH
MCC	–	250/150	5	9 ± 1	79 ± 8	12 ± 1	71	18	3	8
MCC	–	250/150	10	3.0 ± 0.3	84 ± 8	13 ± 1	61	28	–	6
MCC	–	250/300	15	4.0 ± 0.4	91 ± 9	5.0 ± 0.5	43	56	–	–
MCC	–	300/150	5	5.0 ± 0.5	66 ± 7	29 ± 3	66	4	–	30
MCC	–	150–300/150	7	3.0 ± 0.4	73 ± 7	24 ± 3	67	11	18	4
TCC	–	250/150	5	2.0 ± 0.3	50 ± 5	48 ± 5	49	2	41	8
MCC	CeO_2	250/300	15	5.0 ± 0.6	88 ± 9	7.0 ± 0.8	17	22	–	61
		250–280/150	5	2.0 ± 0.3	78 ± 8	20 ± 2	11	27[f]	24	25
MCC	Nb_2O_5	250/300	5	4.0 ± 0.5	87 ± 9	9 ± 1	77	3	20	–
		250–280/150	4	4.0 ± 0.5	71 ± 7	25 ± 3	40	7	26	18
MCC	SiO_2	250/300	5	7.0 ± 0.8	83 ± 8	10 ± 1	30	36	34	–
		250–280/150	6	4.0 ± 0.5	73 ± 7	23 ± 2	31	12	28	16
MCC	HSA-SiO_2	250/300	5	2.0 ± 0.3	83 ± 8	15 ± 2	32	8	0	60
		250–280/150	6	6.0 ± 0.7	70 ± 7	24 ± 3	37	17	26	14
MCC	AlFe-MCM-48	250/300	5	2.0 ± 0.3	88 ± 9	10 ± 1	70	18	4	5
		250–280/150	6	2.0 ± 0.3	65 ± 7	33 ± 3	34	21	29	10

LGO levoglucosenone, *AS* anhydrosugars (DGP and LAC), *AH* aromatic hydrocarbons (xylenes)

[a] 10 % w/w of solid catalyst mixed with fresh cellulose

[b] Maximum power given by the fixed power program

[c] Total time of irradiation

[d] Values expressed as average of 3–4 measurements with their analytical errors

[e] Furan compounds

[f] Composition: 20 % of LG and 7 % of DGP

affected respect to the first catalytic pyrolysis experiment. By contrary, after the second calcination, a deep decrease of liquid fraction and a clear increment of gas products were obtained. The analysis of the bio-oil showed a great formation of aromatic hydrocarbons with a depleted amount of LG. These results indicated a strong degradation of the cellulose to give volatile compounds providing evidence of apparent loss of selectivity towards anhydrosugar formation. Taking into account these results, CeO_2 and, to a lesser extent, SiO_2 can be considered as good catalytic materials after one regeneration process, regarding the formation of bio-oil and LG as the main component.

Microwave-induced pyrolysis of cellulose

In order to evaluate the integral effect of the microwave irradiation on the degradation of cellulose, the microwave-induced pyrolysis of cellulose both in the presence and absence of catalysts were performed. In this case the experiments were carried out in a CEM microwave cavity oven by placing the cellulose samples in a quartz reactor, which was located inside the microwave cavity using a sealed irradiation system. Experimental conditions and results are shown in the Table 5.

For catalytic and non-catalytic process, the liquid fraction was reduced greatly in the microwave-assisted pyrolysis compare to the fast pyrolysis reactions, giving no more than 9 % of yield. The longer residence time of products in the microwave reactor favoured the formation of char (>50 %) and gas products. The GC–MS analyses of bio-oils showed furan compounds, xylenes, LGO and other anhydrosugars as main components.

For microcrystalline cellulose the increment of temperature as well as the irradiation time did not improve the amount of bio-oil favouring the formation of gas products. The main differences observed in microwave reactions of MCC compared to the fast

pyrolysis, were the substantial production of LGO, a practical non-existent formation of LG and, in some cases, a high production of furan derivatives. In view of these results, microwave-irradiation promoted the dehydration of LG to give LGO in these static and long residence time pyrolysis reactions. Also, in the reaction of acid pre-treated cellulose LGO and furans were the main constituents of the bio-oil, although a large degradation of the cellulosic material was evidenced through the high yields of gas products (48 %). During the catalytic microwave induced pyrolysis the ring scission of microcrystalline cellulose caused the formation of the same products. It is noted that irradiation conditions affected the catalytic performance of catalysts. Thus, for ceria the increment of power irradiation at 250 °C promoted the formation of xylenes in high yields. This selectivity was lost when the temperature was increased to 280 °C keeping irradiation at only 150 W. A similar trend was found for SiO_2-catalysed reactions, although in this case the amount of LGO was higher than ceria-catalysed experiments. In both silica-catalysed reactions the amount of LGO was similar displaying an analogous performance at 250–280 °C using 150 W of irradiation power.

According to the results, only Nb_2O_5 and Al–Fe-MCM-48 provided high LGO yields (70–77 %) probably as a result of the high acidity displayed by these materials. In this context, ceria, a catalyst with acid properties did not promote LGO formation; furthermore LG was detected in appreciable amount (20 % yield) in the pyrolysate indicating the lower dehydration of this compound under these thermal conditions.

Conclusions

- Fast pyrolysis of MCC at 400 °C gave rise to a large amount of bio-oil enriched in LG while pyrolysis of TC produced poor yields of bio-oil.
- Catalysts promoted the formation of bio-oil in the pyrolysis of MCC at 300 °C (100 °C less than un-catalysed reactions) keeping high selectivity to LG formation.
- In the catalytic reactions of TC, liquid products did not significantly increase respect to the un-catalysed pyrolysis. MCM-48 materials and HSA-SiO_2 displayed a remarkable selectivity to the formation of LGO.
- The application of microwave irradiation could not provide an efficient production of bio-oil.

Acknowledgments The authors gratefully acknowledge financial support of CONICET and SECYT-UNC. Authors also thank Prof. A. Blanc, Prof. R. Carbonio, Dr. G. Lener and Dr. Cecilia Blanco for their contribution in the XRD analysis of cellulose samples and catalysts.

References

Antal MJ (1982) Biomass pyrolysis: a review of the literature. Part I. Carbohydrate pyrolysis. In: Boer KW, Duffie JA (eds) Advances in solar energy, vol I. American Solar Energy Society, Boulder, pp 61–111

Antal M, Varhegyi G (1995) Cellulose pyrolysis kinetics: the current state of knowledge. Ind Eng Chem Res 34:703–717

Bore M, Mokhonoana M, Ward T, Coville N, Datye A (2006) Synthesis and reactivity of gold nanoparticles supported on transition metal doped mesoporous silica. Microporous Mesoporous Mater 95:118–125

Bridgwater A, Grassi G (1991) Biomass pyrolysis liquids upgrading and utilisation. Elsevier Applied Science, England

Choi S-S, Kim M-C, Kim Y-K (2011) Influence of silica on formation of levoglucosan from carbohydrates by pyrolysis. J Anal Appl Pyrolysis 90:56–62

Cid R, Pecchi G (1985) Potentiometric method for determining the number and relative strength of acid sites in colored catalysts. Appl Catal 14:15–21

Covarrubias R, Quijada R, Rojas R (2009) Synthesis of nano-sized ZSM-2 zeolite with potential acid catalytic properties. Microporous Mesoporous Mater 117:118–125

Czernik S, Bridgwater A (2004) Overview of applications of biomass fast pyrolysis oil. Energy Fuels 18:590–598

Diez A, Graziano-Mayer M, Radivoy G, Volpe M (2014) Suzuki-Miyaura cross-coupling of aryl iodides and phenylboronic acid over palladium-free CeO2 catalysts. Appl Catal A 482:24–30

Dobele G, Rossinskaja G, Telysheva G, Meier D, Faix O (1999) Cellulose dehydration and depolymerization reactions during pyrolysis in the presence of phosphoric acid. J Anal Appl Pyrolysis 49:307–317

Dobele G, Meier D, Faix O, Radtke S, Rossinskaya G, Telysheva G (2001) Volatile products of catalytic flash pyrolysis of celluloses. J Anal Appl Pyrolysis 58(59): 453–463

Dobele G, Dizhbite T, Rossinskaja G, Telysheva G, Meier D, Radtke S, Faix O (2003) Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis: a promising method for obtaining 1,6-anhydrosaccharides in high yields. J Anal Appl Pyrolysis 68–69:197–211

Fabbri D, Torri C, Baravelli V (2007) Effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose: an analytical study. J Anal Appl Pyrolysis 80:24–29

Furneaux R, Mason J, Miller I (1988) A novel hydroxylactone from the Lewis acid catalysed pyrolysis of cellulose. J Chem Soc Perkin Trans 1:49–51

Garcia E, Tonetto G, Sanchez M, Volpe M (2005) Preparation of USY zeolite image supported catalysts from $V(AcAc)_3$ and NH_4VO_3. Catalytic properties for the dehydrogenation of *N*-butane in oxygen-free atmosphere. J Colloid Interface Sci 292:179–185

Ioelovich M, Tupureine A, Veveris G (1989) Investigation of the crystalline structure of cellulose in plant materials. Khimija Drev 5:3–9

Jha R, Shylesh S, Bhoware S, Singh A (2006) Oxidation of ethyl benzene and diphenyl methane over ordered mesoporous M-MCM-41 (M = Ti, V, Cr): synthesis, characterization and structure–activity correlations. Microporous Mesoporous Mater 95:154

Kong Y, Jiang S, Wang J, Wang S, Yan Q, Lu Y (2005) Synthesis and characterization of Cu–Ti–MCM41. Microporous Mesoporous Mater 86:191

Li X, Zhang H, Li J, Su L, Zuo J, Komarneni S, Wang Y (2013) Improving the aromatic production in catalytic fast pyrolysis of cellulose by co-feeding low-density polyethylene. Appl Catal A 455:114–121

Lu Q, Xiong W, Li W, Guo X, Zhu X (2009) Catalytic pyrolysis of cellulose with sulfated metal oxides: a promising method for obtaining high yield of light furan compounds. Bioresour Technol 100:4871–4876

Mosier N, Wyman C, Dale B, Elander R, Lee Y, Holtzapple M, Ladisch M (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 96:673–686

Motasemi F, Afzal M (2013) A review on the microwave-assisted pyrolysis technique. Renew Sustain Energy Rev 28:317–330

Oknishi A, Katö K, Hori T, Nakayama M (1981) Crystal structure and ^{1}H- and ^{13}C-n.m.r. studies of 1,4:3,6-dianhydro-α-d-glucopyranose obtained from pyrolysis of cellulose. Carbohydr Res 96:161–166

Orozco A, Ahmad M, Rooney D, Walker G (2007) Dilute acid hydrolysis of cellulose and cellulosic bio-waste using a microwave reactor system. Process Saf Environ Prot 85(B5):446–449

Paine J, Pithawalla Y, Naworal J (2008) Carbohydrate pyrolysis mechanisms from isotopic labeling: part 2. The pyrolysis of D-glucose: general disconnective analysis and the formation of C1 and C2 carbonyl compounds by electrocyclic fragmentation mechanisms. J Anal Appl Pyrolysis 82:10–41

Pikorz J, Radlein D, Scott D (1986) On the mechanism of the rapid pyrolysis of cellulose. J Anal Appl Pyrolysis 9:121–137

Rutkowski P (2012) Pyrolytic behavior of cellulose in presence of montmorillonite K10 as catalyst. J Anal Appl Pyrolysis 98:115–122

Shafizadeh F, Furneaux R, Stevenson T, Cochran T (1978) Acid-catalyzed pyrolytic synthesis and decomposition of 1,4:3,6-dianhydro-α-D-glucopyranose. Carbohydr Res 61:519–528

Shaik S, Sharratt P, Tan R (2013) Influence of selected mineral acids and alkalis on cellulose pyrolysis pathways and anhydrosaccharide formation. J Anal Appl Pyrolysis 104:234–242

Shen D, Gu S (2009) The mechanism for thermal decomposition of cellulose and its main products. Bioresour Technol 100:6496–6504

Shra'ah A, Helleur R (2014) Microwave pyrolysis of cellulose at low temperature. J Anal Appl Pyrolysis 105:91–99

Tonetto G, De Lasa H, Volpe M (2004) Butane dehydrogenation on vanadium supported catalysts under oxygen free atmosphere. Appl Catal A 272(1-2):69–78

Torri C, Giorgio Lesci I, Fabbri D (2009) Analytical study on the pyrolytic behaviour of cellulose in the presence of MCM-41 mesoporous materials. J Anal Appl Pyrolysis 85:192–196

Vinu R, Broadbelt L (2012) A mechanistic model of fast pyrolysis of glucose-based carbohydrates to predict bio-oil composition. Energy Environ Sci 5:9808–9826

Wang X, Chen H, Luo K, Shao J, Yang H (2008) The influence of microwave drying on biomass pyrolysis. Energy Fuels 22:67–74

Xu J, Luan Z, He H, Zhou W, Kevan L (1998) A reliable synthesis of cubic mesoporous MCM-48 molecular sieve. Chem Mater 10:3690–3698

Yin C (2012) Microwave-assisted pyrolysis of biomass for liquid biofuels production. Bioresour Technol 120:273–284

Zhang J, Zhang J, Lin L, Chen T, Zhang J, Liu S, Li Z, Ouyang P (2009) Dissolution of microcrystalline cellulose in phosphoric acid- molecular changes and kinetics. Molecules 14:5027–5041

Zhao H, Kwak J, Zhang Z, Brown H, Arey B, Holladay J (2007) Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis. Carbohydr Polym 68:235–241