

# A new Star(ch) is born: Starbons® as biomass-derived mesoporous carbonaceous materials

## El nacimiento de una nueva estrella: Los Starbons® como materiales mesoporosos carbonosos derivados de la biomasa

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### Abstract

Porous carbon materials are present in a wide range of technologically important applications, including separation science, heterogeneous catalyst supports, water purification filters, stationary phase materials, as well as the developing future areas of energy generation and storage applications. Hard template routes to ordered mesoporous carbons are well established, but whilst offering different mesoscopic textural phases, the surface of the material is difficult to chemically post-modify and processing is energy, resource and step intensive. The production of carbon materials from biomass (i.e. sugars or polysaccharides) is a relatively new but rapidly expanding research area. In this manuscript, we describe the preparation, properties and applications of a novel family of polysaccharide-derived mesoporous carbonaceous materials derived from renewable resources (namely polysaccharides) denoted as Starbons®.

### Resumen

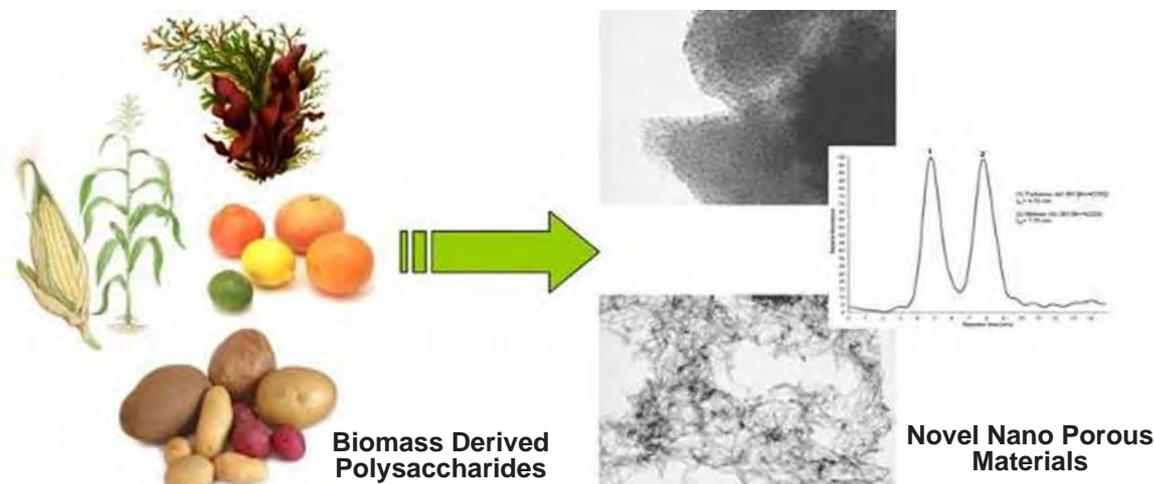
Los materiales carbonosos porosos están presentes en un gran número de aplicaciones relevantes tales como adsorción, catálisis heterogénea (fundamentalmente como soportes), purificación de aguas y cromatografía, así como en áreas de actual desarrollo como en aplicaciones de almacenamiento y producción de energía. Las rutas de producción de carbones mesoporosos utilizando "hard templates" han sido desarrolladas y bien establecidas en los últimos años, aunque a pesar de ofrecer una variedad de fases mesoscópicas y propiedades texturales, la superficie del material obtenido es relativamente difícil de modificar químicamente, requiriendo en todos los casos de una serie de tratamientos intensivos y/o multi paso. La producción de carbones a partir de biomasa (por ejemplo a partir de azúcares y/o polisacáridos) es un área de conocimiento

relativamente nueva que está experimentando un auge importante en años pasados. En este artículo, se detalla la síntesis, propiedades y aplicaciones de una nueva familia de materiales carbonosos derivados de la biomasa (principalmente polisacáridos) llamados Starbons®.

### Introduction

Pressures of an evolving sustainable society are encouraging and developing awareness amongst the materials science community of a need to introduce and develop novel porous media technology utilising benign, resource efficient and environmentally sound methodologies. In this regard, the preparation of porous materials from renewable resources is a relatively new area of knowledge which is quickly being recognised not only in terms of application/economic advantages but also with regard to a holistic sustainable approach to useful porous media synthesis. The main inhibitor to the development of this approach is the "soft" mechanical/chemical resistance of native biomass derived materials.

Recent research from our groups as well as other national and international authors has focused on the transformation of nanostructured forms of polysaccharide biomass into more stable porous carbonaceous forms for high value applications (summarised in Schemes 1 and 2) [1, 2]. The proposed methodology can open routes to the production of various differently structured porous materials including promising novel families of carbonaceous materials and highlight a green alternative to traditional materials based on templating methods. The principle of our research in this area relies on the generation of porous polysaccharide precursors which can then be carbonised to preserve the porous structure (Scheme 1).



**Scheme 1.** Transformation of non-porous native polysaccharide into useful porous carbonaceous materials. Reproduced by permission of the Royal Society of Chemistry.

**Esquema 1.** Transformaciones de polisacáridos no porosos en materiales carbonosos porosos. Reproducida con permiso de la Royal Society of Chemistry.

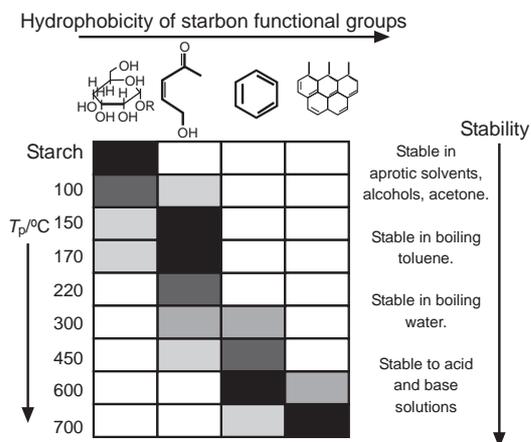
This material synthesis strategy was initially focused on the use of mesoporous forms of the composite polysaccharide starch, but is evolving into potentially a generic/universal tuneable polysaccharide-based route. The technology involves:

1. Native polymer expansion (the key process stage), via polysaccharide aqueous gel preparation.
2. Production of solid mesoporous polysaccharide, via solvent exchange/drying
3. Thermal carbonisation/dehydration

The resulting carbon-based materials are highly porous and mechanically stable in the 150 to 1000°C temperature range. The carbonisation process renders robust mesoporous carbonaceous materials at temperature above 700°C with a wide range of technologically important applications, in areas including heterogeneous catalysis, water purification, separation media as well as energy generation and storage (e.g. fuel cell electrodes/batteries) (Scheme 2).

The first member of this novel family of porous carbon based materials derived from porous starch was defined under the patented and trademark name "Starbon®" [1, 2]. The stability of these polysaccharide-derived mesoporous materials at temperatures below 700°C leads to porous carbonaceous materials with tuneable surface, textural and morphological properties, dependent on the carbonisation temperature employed and the polysaccharide used as a the precursor (Figure 1). A transition from a polysaccharide rich at low carbonisation temperatures (here using starch as example) through to an increasingly more polyaromatic graphitic-like structure (as carbonisation temperatures approach 700°C) can be clearly observed in the preparation of these materials. Similarly, there is a progressive increase in the hydrophobicity of the surface functionality present. Starbons® prepared in the temperature range: 100-700°C, present accessible surface functionality ideal for chemical modification (e.g. silylation, alkylation, esterification, etherification, amination), allowing post functionalisation strategies to further manipulate their physical and chemical properties; arguably

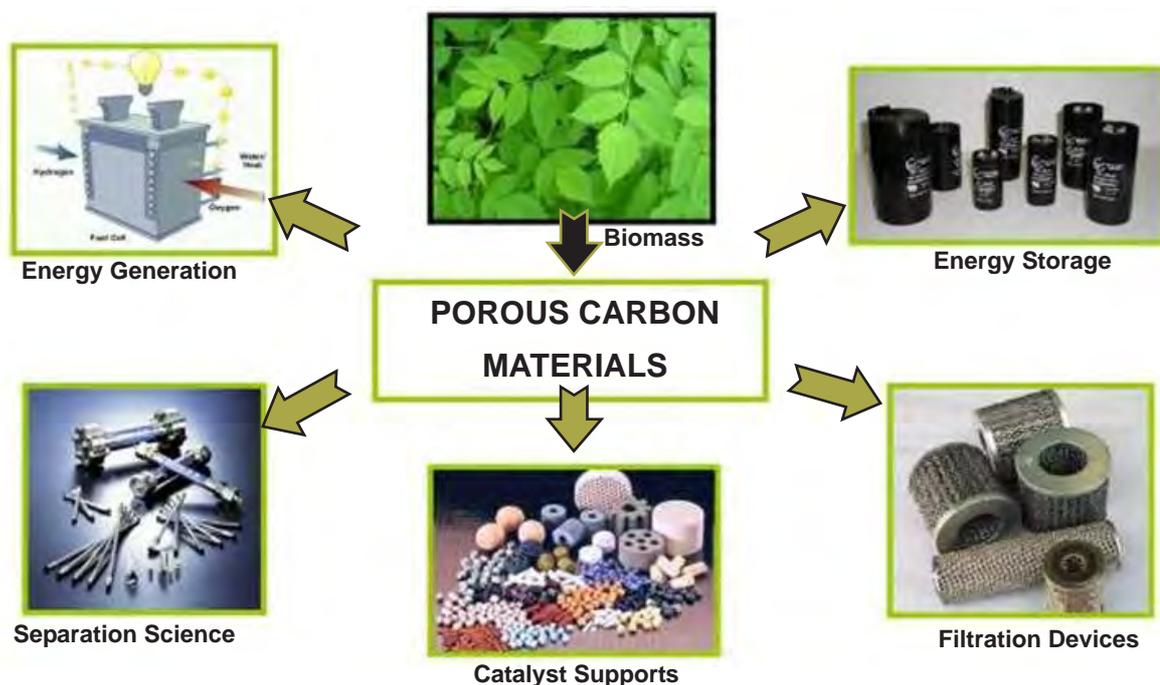
features not typically encountered in the synthesis of other porous carbons.



**Figure 1.** Distribution of functional groups on Starbons® prepared at different temperatures: color scale to indicate relative amounts of different groups (black represent highest).  $T_p$  = temperature of Starbon® preparation. Reproduced by permission of the Royal Society of Chemistry.

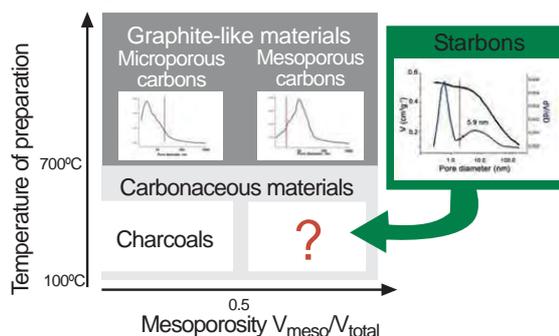
**Figura 1.** Distribución de los grupos funcionales en materiales Starbon® preparados a distintas temperaturas, indicando las proporciones de los diferentes grupos (en negro se representa la mayor concentración).  $T_p$  = temperatura de preparación de los materiales Starbon®. Reproducida con permiso de la Royal Society of Chemistry.

Furthermore, the distinctive features of Starbons® including the tuneability of chemical properties between the original precursor polysaccharides (e.g. starch; high oxygen surface content) and a more classical carbon surface Starbons® effectively combine the surface accessibility of mesoporous carbons with the complex chemistry of charcoals (Fig. 2). The lack of a template avoids wasteful processing steps and harmful chemicals and allows materials to be prepared at a temperature of choice (e.g. 200–1000°C). These materials also exhibit outstanding mesoporous textural properties, with pore volumes and sizes equal to materials prepared via conventional carbonisation and/or hard template routes. The flexibility in terms of carbonisation temperature, provided the possibility of tuneable



**Scheme 2.** Current and potential applications of biomass derived carbons. Reproduced by permission of the Royal Society of Chemistry. **Esquema 2.** Aplicaciones actuales y potenciales de materiales carbonosos porosos derivados de la biomasa. Reproducida con permiso de la Royal Society of Chemistry.

surface chemistry, arguably a material feature not accessible via hard templating that relies on high temperature carbonisation ( $> 700^{\circ}\text{C}$ ), or soft templating based on the self assembly and polymerisation gel properties of aromatic precursors (e.g. resorcinol), chemically limiting the post processing surface functionality available.



**Figure 2.** Potential of polysaccharide-derived Starbon® materials with regard to porous structure compared to common porous carbon materials. Insets show the different pore size distributions marking with a red vertical line the limit between micro- (left side) and mesoporosity (right side). Reproduced by permission of the Royal Society of Chemistry.

**Figura 2.** Potencial de los materiales Starbon® y su estructura porosa con respecto a los carbones convencionales. La figura correspondiente a los Starbons representa la distribución del tamaño de poro que marca con una línea roja vertical el límite entre los micro- (parte izquierda) y los mesoporos (parte derecha). Reproducida con permiso de la Royal Society of Chemistry.

### Starbons preparation

A simple and efficient acid-catalysed thermal conversion of mesoporous starch-derived materials into stable nanostructured, porous carbonaceous materials allows the low to high temperature generation of Starbons® as shown in Figure 3. Starbon® production comprises of three main stages (Scheme 3) [1-3].

Starch (typically from high amylose corn starch) is gelatinised by heating in water [1 g: 20 mL (w/v ratio)]. The resulting viscous solution is cooled to  $5^{\circ}\text{C}$  for typically one to two days to yield a porous gel. Water in the gel is subsequently exchanged with

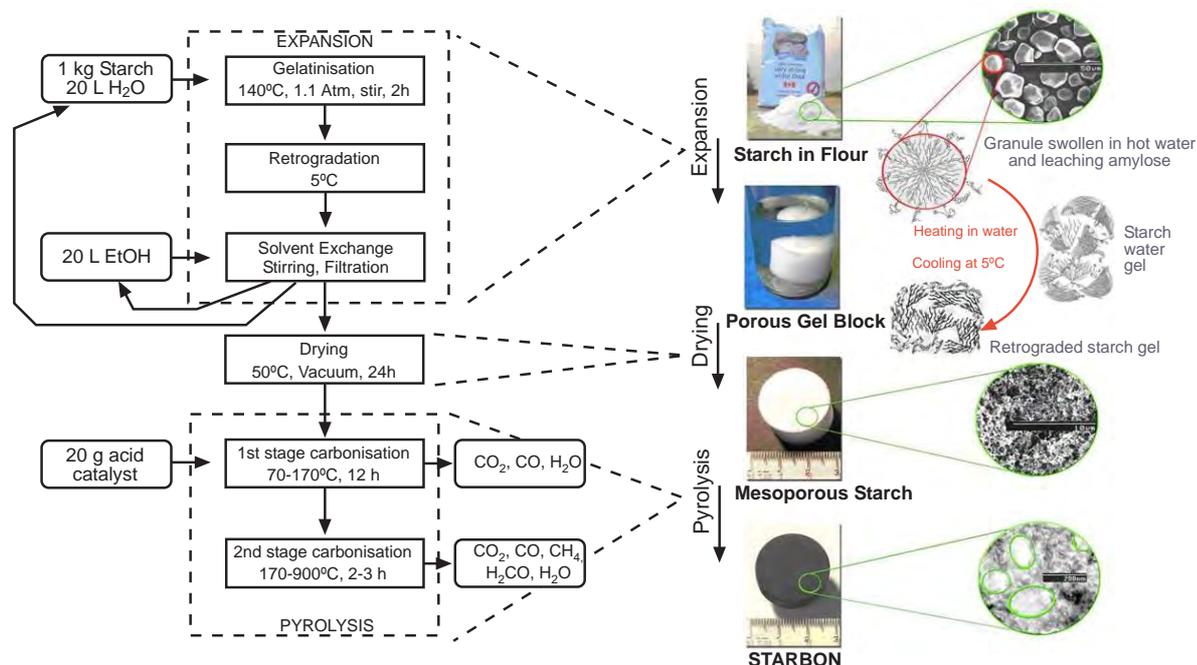
the lower surface tension solvent ethanol. The resulting material is then filtered and may be oven dried to yield a predominantly mesoporous starch with a surface area of typically  $180\ 200\ \text{m}^2\text{g}^{-1}$ .<sup>27</sup> In the final stage the mesoporous starch is doped with a catalytic amount of an organic acid (e.g. *p*-toluenesulfonic acid) and heated under vacuum [1, 3].

### Physico-chemical and textural properties of Starbon Materials

The porous structure of the starch precursor is preserved in the Starbon® materials overcoming issues of micelle collapse encountered in polymer templated methods for the synthesis of mesoporous carbons. The proposed methodology also eliminates the need for mesoporous templates such as silica to define the structure. SEM images illustrate that the granular morphology of mesoporous starch can be maintained during pyrolysis with only minor changes due to shrinkage (Figure 3). The porous/textural properties of starch-derived Starbons® were characterised via  $\text{N}_2$  sorption studies (Table 1).

The total pore volume and the average pore diameter in the mesoporous region remain essentially constant throughout the carbonisation process. The average pore diameter was found in the mesoporous region (ca. 10 nm), indicating a predominance of mesopores. Although there is a substantial increase in the microporous region contribution to the total surface area, the actual microporous volume is small in comparison to the total mesoporous volume (Table 1).

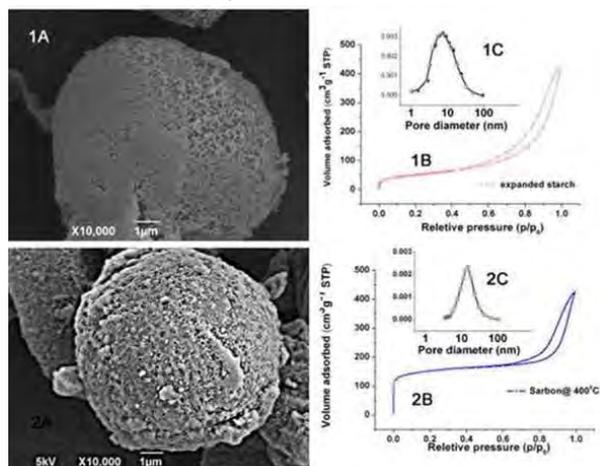
The surface energy,  $E_{\text{DR}}$ , (from the Dubinin-Radushkevich model) demonstrates an overall increase as the carbonisation preparation temperature rises. More starch-like properties are retained until ca.  $150^{\circ}\text{C}$ , above which there is gradual change towards increasingly carbon-like properties [1, 3]. X-ray photoelectron spectroscopy (XPS) of the material surface further supports these observations indicating a nearly linear increase of carbon/oxygen ratio on the surface from 1.2 for



**Scheme 3.** Diagrammatic representation of the main processing steps in the production of starch-derived Starbon® materials. Reproduced by permission of the Royal Society of Chemistry.

**Esquema 3.** Esquema de los pasos clave en la producción de materiales Starbon® a partir de almidón. Reproducida con permiso de la Royal Society of Chemistry.

expanded starch to 8.5 for Starbon® prepared at 800°C (Table 1). This carbonisation behaviour is also reflected in elemental analysis data, although the ratios are slightly lower for the bulk than for the surface. This analytical information confirmed our initial assertions that the carbonisation mechanism is initiated at the outer material surface progressing to the inner bulk; i.e. initial acid catalyst adsorption at the surface and pore walls.



**Figure 3.** SEM images of mesoporous starch precursor (1A) and Starbon® material derived therefrom (2A), demonstrating maintenance of morphology and textural properties (1C→2C). Reproduced by permission of the Royal Society of Chemistry. **Figura 3.** Fotografías SEM del precursor de almidón mesoporoso (1A) y del Starbon® derivado del mismo (2A), que demuestran que los Starbon® preservan la morfología y las propiedades texturales (1B a 2C) del polisacárido mesoporoso de partida. Reproducida con permiso de la Royal Society of Chemistry.

A greater carbon-like character imparted increased thermal stability. Thermogravimetric analysis demonstrated that when heated, Starbons® degraded to a lesser extent than the parent starches (i.e. 90 % and 23 % percent weight loss for starch and Starbon® prepared at 450°C respectively). Changes in chemical functionality that occurred during Starbon® preparation were also investigated by <sup>13</sup>C CP MAS NMR analysis. Three main chemical changes in the transition from starch to Starbon® were found. In the first step (i.e. 150–200°C), starch backbone CH<sub>2</sub>OH groups condensed to form ether groups. In the second step (i.e. 200–300°C) residual CH<sub>2</sub>OH groups condensed, coupled with glycosidic ring opening, to produce carbonyl groups conjugated with olefinic groups, generating increased aliphatic and alkene/aromatic character ( $\delta = 20\text{--}50$  ppm). In the final step, at carbonisation temperatures > 300°C,

the aliphatic groups are gradually converted to extended aromatic  $\pi$  systems ( $\delta = 115\text{--}140$  ppm).

A progressive decrease in the concentration of CH<sub>2</sub>OH groups was also observed via diffuse reflectance FTIR spectroscopy (spectra not shown), concurrently with an increase in the aliphatic and finally aromatic functionalities [4]. These changes are similar to those reported previously for ordinary starch, but here decomposition occurred at much lower temperatures [5].

## Applications of Starbon materials

### Heterogeneous catalysed processes

Simple treatment of starch-derived Starbon® materials with sulfuric acid provided a series of porous solid Brønsted acids that were shown to be efficient catalysts under a range of conditions including dilute aqueous solutions in a wide range of acid catalysed processes including esterifications of organic acids in aqueous medium, acylations of alcohols and amines, and alkylations of aromatics [6–8]. These solid acids, containing similar SO<sub>3</sub>H loadings (0.4 - 0.5 mmol g<sup>-1</sup>) [6–8], exhibited remarkably different activities in esterifications, amidations and redox chemistries.

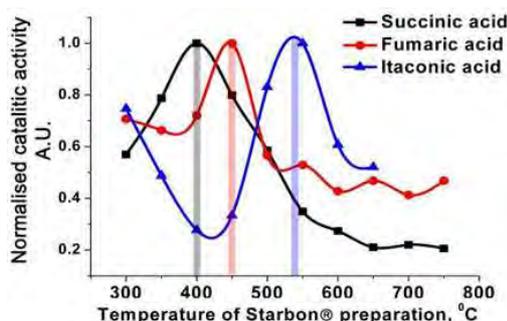
Esterifications are one of the most useful transformations in Organic Synthesis. However, they are largely carried out in organic solvents due to the high sensitivity to aqueous environments as water can hydrolyse the ester back to the acid. Starbon® acids were considered at this point to be an interesting alternative to the already reported acid catalysts. Our novel aqueous catalytic chemistry relied on the ability to adjust the surface properties and hydrophobicity/hydrophilicity balance of mesoporous Starbons® to achieve highly active, selective and reusable water-tolerant solid acids. We focused our investigations on diacids derived from fermentation. The esters of such diacids find use in the manufacture of polymers, fine chemicals, perfumes, plasticisers and solvents. Different substrates (e.g. succinic (SA), fumaric, levulinic and itaconic acids) were successfully esterified in aqueous ethanol, providing high conversions and selectivities to their respective esters [7, 8]. The rates of esterification of diacids (succinic, fumaric and itaconic) were found to be between 5–10 times higher for our Starbon® acids compared to those of commercial solid acids (e.g. zeolites, sulfated zirconias, acidic clays and resins) or microporous commercial sulfonated carbons (DARCO® and NORIT®) [2, 6, 7]. Starbon® acids were also found to have a temperature dependent

**Table 1:** Physical analysis of starch and starch-derived Starbon® materials.

**Tabla 1:** Propiedades físicas del almidón y de los materiales derivados de almidón Starbon®.

Material	Surface Area m <sup>2</sup> g <sup>-1</sup>		Pore Volume cm <sup>3</sup> g <sup>-1</sup>		C/O atomic ratio		Surface Energy EDR <sup>d</sup> kJ mol <sup>-1</sup>	Pore diameter (nm)
	SBET	Mesoporous	Total	Mesoporous	EA	XPS		
Mesoporous Starch	184	160	0.62	0.61	1.20	1.10	7.4	7.6
Acid/doped Mesoporous Starch	230	170	0.67	0.66	1.20	1.30	8.2	8.6
Starbon@100°C	179	171	0.67	0.61	1.26	1.34	6.9	10.5
Starbon@150°C	172	137	0.68	0.58	1.55	1.99	6.5	10.4
Starbon@220°C	151	90	0.57	0.42	2.71	2.73	10.5	16
Starbon@300°C	293	60	0.53	0.37	3.43	3.79	17.7	17.2
Starbon@350°C	332	65	0.56	0.38	5.00	5.10	18.2	16.8
Starbon@450°C	475	70	0.52	0.32	6.01	6.04	20.6	14.5
Starbon@600°C	528	153	0.62	0.43	7.53	7.55	24.4	12.1
Starbon@700°C	538	158	0.73	0.55	8.54	8.50	26.6	10.6
Starbon@800°C	600	167	0.63	0.43	8.60	8.60	25.8	7.0

optimum of catalytic activity (that could be controlled by the preparation temperature of the parent Starbon® and consequently by modification of its surface properties) as well as a substrate dependent catalytic activity maximum (Figure 5). Starbon® acid activities peaked at ca. 400, 450 and 550°C for succinic, fumaric and itaconic acids, respectively, with sharply reduced activities below or above this preparation temperature.



**Figure 5.** Normalised catalytic activity of Starbon® acids in the esterification of succinic, fumaric and itaconic acids depending of the parent Starbon preparation temperature. Maximum catalytic activities were: Succinic acid (400°C,  $k = 32 \times 10^{-5} \text{ s}^{-1}$ ); Fumaric acid (450°C,  $k = 5.0 \times 10^{-5} \text{ s}^{-1}$ ); Itaconic acid (550°C,  $k = 15.4 \times 10^{-5} \text{ s}^{-1}$ ). Reproduced by permission of the Royal Society of Chemistry.

**Figura 5.** Actividad catalítica normalizada de los Starbon®-SO<sub>3</sub>H en la esterificación de los ácidos succínico, fumárico e itacónico dependiendo de la temperatura de preparación de los Starbon®. La actividades catalíticas máximas fueron: Ácido Succínico (400°C,  $k = 32 \times 10^{-5} \text{ s}^{-1}$ ); Ácido fumárico (450°C,  $k = 5.0 \times 10^{-5} \text{ s}^{-1}$ ); Ácido itacónico (550°C,  $k = 15.4 \times 10^{-5} \text{ s}^{-1}$ ). Reproducida con permiso de la Royal Society of Chemistry.

The efficient and atom economic preparation of aromatic amides via N-acylation of amines was also successfully carried out using sulfonated Starbons® as heterogeneous catalysts under microwave irradiation. Quantitative conversions of starting material were typically achieved in 5-15 min with very high selectivities to the target product (Table 2), applicable to a wide range of compounds (including aromatic and aliphatic amines), substituents and acids. Starbon® acids also provided remarkably improved activities compared to other commercial solid acid catalysts including zeolites, Al MCM 41 and acidic clays [8].

**Table 2:** N-Acylation of a range of amines with acetic acid using Starbon®-400-SO<sub>3</sub>H as catalyst and acetic acid as acylating agent under microwave irradiation<sup>a</sup> from reference 47. Reproduced by permission of the Royal Society of Chemistry.

**Tabla 2:** N-Acilación de un rango de aminas con ácido acético usando Starbon®-400-SO<sub>3</sub>H como catalizador y ácido acético como agente acilante bajo radiación microondas<sup>a</sup> de la referencia 47. Reproducida con permiso de la Royal Society of Chemistry.

Entry	Substrate	Product	Time (min)	Conversion <sup>c</sup> (mol%)	S <sub>product</sub> (mol%)
Blank <sup>b</sup>			15	<10	>98
1			10	90 (87)	>99
2			2	>99 (95)	>99
3			5	87 (79)	>99
4			0.6	>99 (94)	>98
5			1	>99 (92)	>99
6			15	77	>99
7			15	82	>95

<sup>a</sup> 2 mmol substrate, 2 mmol AcOH, 0.1 g Starbon-400-SO<sub>3</sub>H, microwave, 300 W (maximum power output), 130 °C (maximum temperature reached); <sup>b</sup> Blank reaction in the absence of catalyst; <sup>c</sup> Isolated yields, where appropriate, are given in brackets

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## References

- Luque R, Macquarrie DJ, Budarin VL, Clark JH, Milkowski K, White RJ, US Patent 2009/0078913 A1.
- White RJ, Budarin VL, Luque R, Clark JH, Macquarrie DJ, Tuneable porous carbonaceous materials from renewable resources, Chem. Soc. Rev. 2009; 38(12):3401-3418.
- Budarin V, Clark JH, Hardy JJE, Luque R, Macquarrie DJ, Milkowski K, Tavener SJ, Wilson AJ, Starbons: new starch-derived mesoporous carbonaceous materials with tunable properties, Angew. Chem. Int. Ed. 2006, 45:3782-3786.
- Lua AC, Yang T, J. Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell, Colloid Interface Sci. 2004, 274:594-601.
- Zhang X, Golding J, Burgar I, Thermal decomposition chemistry of starch studied by <sup>13</sup>C high-resolution solid-state NMR spectroscopy, Polymer 2002, 43:5791-5796.
- Budarin V, Luque R, Clark JH, Macquarrie DJ, Versatile mesoporous carbonaceous materials for acid catalysed reactions, Chem. Commun. 2007, 524-526.
- Budarin VL, Luque R, Macquarrie DJ, Clark JH, Towards a bio-based industry: benign catalytic esterifications of succinic acid in the presence of water, Chem. Eur. J. 2007, 13:6914-6919.
- Luque R, Budarin V, Clark JH, Macquarrie DJ, Microwave-assisted preparation of amides using a stable and reusable mesoporous carbonaceous solid acid, Green Chem. 2009, 11:459-461.