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Synthesis of beta silicon carbide powders from biomass gasification residue

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Abstract The synthesis of beta silicon carbide (β-SiC) powders by carbothermal reduction of silica with carbon in a high temperature tube furnace was investigated. As carbon source, fine carbon-containing char from biomass gasification was used, in order to verify the feasibility of producing a high added value material starting from waste residue, and to promote the gasification processes as alternative route of energy production by the proper by-products exploitation. Starting mixture was prepared by mechanically mixing silica and char in the weight ratio of SiO_2:C of 1.514; the mixture then reacted in a tube furnace at temperature of 1,550 °C at different residence times (1, 1.5, 2 and 2.5 h), at a constant flow rate of 0.8 $dm^3\ min^{-1}$ of argon. The reaction products were characterised with XRD, FTIR spectroscopy and transmission electron microscopy (TEM). The process turned out to be capable of producing high quality SiC powders, suitable for making ceramic materials and composites; the product shows an uniform spherical shape, a very fine particle size (within the range of 30–100 nm) and a purity degree varying from 70% to 95%, depending on the residence time.

Introduction

Thermochemical treatments, like pyrolysis and gasification, applied on biomass and waste, are a promising way for alternative energy production [1, 2]. Typically, both processes produce three fractions, gas, oils and char, whose corresponding amounts and composition depend upon the process parameters [3, 4].

While the first two fractions, gas and oils, seem to be suitable as energy vectors [5, 6], the last fraction, the char, that is the solid by-product, shows some management problems and its final destination affects widely the global economic balance of the process.

In order to overcome this limit and to achieve a fruitful char employment, many efforts have been put to explore different ways of utilisation.

Direct applications of char as activated carbon [7–10] or solid fuel [11] could be possible because of its high carbon content.

In a different approach char could be seen as a low-cost carbon source, able to replace coal in chemical reactions. Within this framework, synthesis via carbothermal reduction could open a new way for high added value applications of the char [12, 13]; in fact this class of reactions actually plays an important role in ceramic powders synthesis [14–16], like SiC, Si_3N_4, TiC, NbC, etc.

Silicon carbide (SiC) is one of best materials for advanced applications [17–20]. Its peculiars properties, such as high hardness and strength, excellent corrosion/oxidation resistance, good high-temperature strength and high thermal conductivity, makes it an optimal choice as reinforcement for ceramic composites [21].

Silicon carbide powders can be produced in three principal ways: pyrolysis of silane compounds [22], direct

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carbonisation of Si metal [23], and, of course, carbothermal reduction of SiO_2.

The first method uses a very high cost silicon source, while Chemical Vapour Deposition (CVD) from silane is expensive and hazardous for the nature of precursor employed. These two methods produce high-purity SiC powders for specific technical applications and they are used for composite materials (i.e., Carbon Fibres) infiltration.

The third method is the cheapest one: it starts from inexpensive silicon dioxide and carbon (or carbon source) that usually react at temperature ranging from 1,400–2,100 °C to give SiC. The SiC phase depends on synthesis temperature; typically, at low temperature (below 1,400 °C) β-phase prevails whereas α-SiC is the principal phase at higher temperature (up to 2,100 °C).

The synthesis is described from the equation [24, 25]:

$$SiO_2(s) + 3C(s) \Leftrightarrow SiC(s) + 2CO(g) \qquad (1)$$

The reaction mechanism is not completely explained, but it is commonly accepted that the carbothermal reduction proceeds in the following fundamental steps:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \qquad (2)$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \qquad (3)$$

First the reaction generates the gaseous SiO which subsequently reacts with carbon to form the final product. The constant removal of CO from the reaction environment is required to cause the overall reaction (1) to proceed in the favourable direction of SiC production; nevertheless step (3) is a solid–gas reaction, then high partial pressure of SiO (g) is desirable in order to achieve higher yield of SiC [26, 27].

Hence, the intimate contact of silica and carbon widely affects the formation of SiC [25]. On the other hand, the morphology and the size of the SiC produced seem to depend upon the characteristics (surface area, granulometry) of the carbon precursor [28, 29].

Recent developments in technical applications empatise the role of the starting materials: new applications in the field of ceramic reinforced composites show the improvements of the mechanical properties using nanometer range SiC particles (nanocomposites) [30].

Consequently, economical and efficient synthesis routes for nanometer-sized SiC powders are getting more and more important [31].

This work concerns the synthesis of silicon carbide powder, using char from biomass gasification and silica as starting materials, by carbothermal reduction process. The effect of the residence time on the production and the characteristics of SiC powder, together with the results of TEM, XRD and FTIR analysis, will be discussed.

Experimental

Materials

The starting materials were poplar gasification solid residue (char), with an average particle size less than 0.2 µm (proximate and elemental analysis of the char are reported in Table 1), and commercial silica gel (Carlo ERBA silica gel 60 230–400 mesh ASTM).

Poplar gasification process was conducted using the experimental apparatus described in a previous work [32]

Both components were thoroughly mixed in a mixer drum for 2 h, fixing the powder weight ratio SiO_2/C at 1.514 wt. After being ground, samples were maintained under ambient conditions.

Apparatus and procedures

SiC synthesis were conducted on a bench scale tubular furnace (Lenton PTF 15/75/450) at 1,550 °C at different residence time of the powder (see Table 2). Argon flow was appropriately set in order both to be sufficient to remove the CO gas produced in the overall process and to prevent gaseous SiO to be swept away from the hot zone (reactions 2 and 3). Approximately 20 g of material were used for each test, in alumina crucibles.

Table 1 Char proximate and elemental analyses

Proximate analysis	
Moisture	2.00 (by weight)
Volatile	15.07 (by weight)
Fixed carbon	76.16 (by weight)
Ash	6.77 (by weight)
Elemental analysis[a]	
N	0.14 (by weight)
C	85.80 (by weight)
H	1.12 (by weight)
O	6.17 (by difference)

[a] All weight are given on a dry basis

Table 2 Process parameters

Test	Temperature (°C)	Residence time (min)	Argon flow ($dm^3\ min^{-1}$)
S1	1,550	60	0.8
S2	1,550	90	0.8
S3	1,550	120	0.8
S4	1,550	150	0.8

A TA Instrument model TG 2950 system was used to analyse the macro-component composition (proximate analysis) of the starting mixture and to verify the presence of fixed carbon in the synthesis products; pure nitrogen was used as inert purge gas, at a constant flow rate of 100 cm^3 min^{-1}, for proximate analysis, while air was used as oxidizing agent for carbon determination.

Ultimate analysis was obtained with a Thermo Quest EA 1110 analyzer. Such an analysis gives simultaneously the weight percent of carbon, hydrogen, nitrogen and sulphur in the samples; oxygen determination can afterwards be obtained by difference.

Initial ash content was further evaluated by incineration at 1,000 °C.

The heating value of the material was estimated using a bomb calorimeter IKA C5000 in adiabatic modality.

A Nexus Thermo Optek Attenuated Total Reflectance Fourier Transform Infrared (ATR/FT-IR) spectrometer and a FEITEM Morgagni 100 kV Transmission Electron Microscope (TEM) were used for the product characterisation.

The excess carbon was removed from the SiC powder by firing the product in oxidizing atmosphere at 700 °C, whereas the unreacted silica was removed by treating the powder with 50% HF and washing with alcohol.

The influence of the residence time on the products characteristics and on the advancement of the carbothermal reaction was evaluated in terms of conversion, selectivity and yield of both carbon and silica for the different trials, according to the following expressions:

$$c_i = \frac{mol_{i-in} - mol_{i-out}}{mol_{i-in}} \tag{4}$$

$$S_i = \frac{mol_{SiC}}{mol_{i-in} - mol_{i-out}} \tag{5}$$

$$Y_i = \frac{mol_{SiC}}{mol_{i-in}} \tag{6}$$

where ‘i’ stands either for carbon or for silica and ‘in’ and ‘out’ represent the corresponding molar amounts at the beginning and at the end of the reaction.

Consequently:

$$Y_i = c_i \times S_i \tag{7}$$

Results and discussion

Figure 1 shows the distribution of the components into the starting mixture, where dark (silica) and light (carbon) areas are representative of the adequate blending of the reagents, that is an essential requirement for the synthesis: the first reaction step (1) is actually a solid–solid model reaction, whose advancement is clearly dependent upon the intimate surface contact.

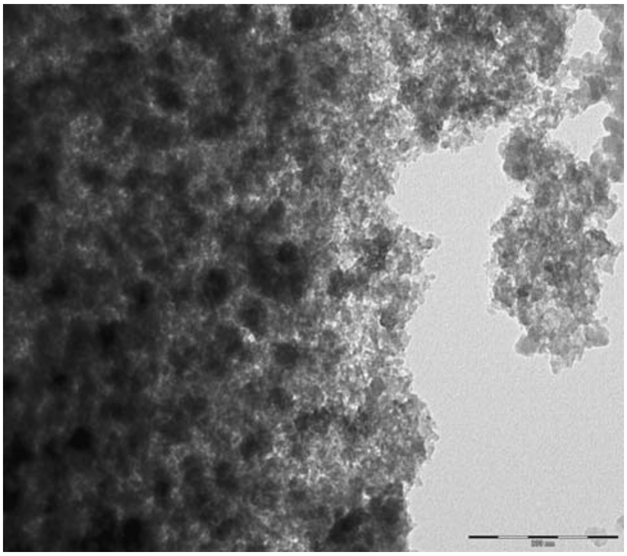


Fig. 1 TEM micrograph of the starting mixture (char + SiO_2)

The proximate and elemental analysis data of the starting mixture are reported in Table 3, while Fig. 2 shows the FTIR spectrum of the starting mixture, performed by means of HATR technique, with the typical signals of silica Si–O bonds at low wavenumber.

The SiO_2/C weight ratio of the mixture, fixed at 1.514, turns out to be slightly lower than the stoichiometric molar ratio of reaction (1), allowing to expect the absence of any free carbon in the synthesis product.

The compositional data of the starting mixture can also be used to calculate the theoretical mass loss value, according to the reaction (1), and the theoretical reaction product composition, that gives a residual amount of silica of 16.7%.

Table 3 Proximate and elemental analysis of starting mixture

Proximate analysis	
Moisture	5.75 (by weight)
Volatile	7.84 (by weight)
Fixed carbon	25.50 (by weight)
Ash from char	2.42 (by weight)
Silica	58.49 (by weight)
Elemental analysis	
N	0.05 (by weight)
C	30.68 (by weight)
H	0.40 (by weight)
O	2.21 (by difference)
Total organic	33.34 (by weight)

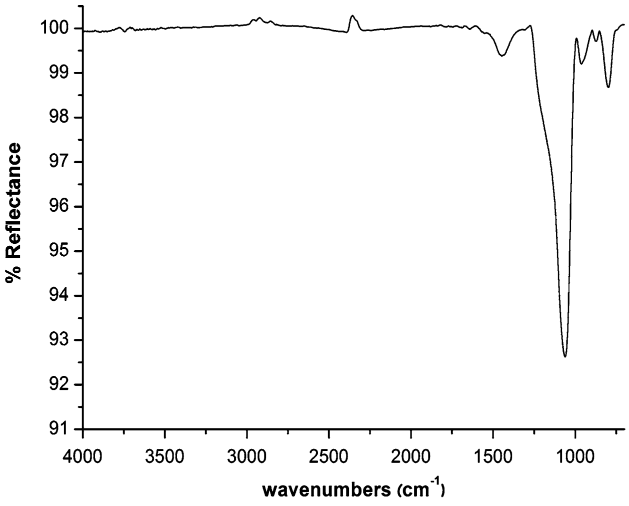


Fig. 2 FTIR spectrum of starting mixture

Calculated weight loss data of the samples at different residence time, as reported in Fig. 3, show instead an increasing weight loss at higher residence time, in accordance with an advancement of the carbothermal reaction. Furthermore weight losses are found to be always higher than the corresponding theoretical value, suggesting a higher silica consumption (and a higher SiO loss), even if at lower residence time (S2 and S1 tests) the difference is not dramatic.

HATR/FT-IR spectra of the products, as compared to the starting mixture (Fig. 4a–e), show that, owing to the synthesis reaction, the wide band at 1,046 cm^{-1} (Si–O) of the silica leaves plenty for the band at 796 cm^{-1} (Si–C); nevertheless, the signal at 1,046 cm^{-1} keeps still visible even progressively lowering with the residence time, because of the presence of non reacted SiO_2 [33–35]; such a signal disappears or is almost negligible only after product purification (combustion at 700 °C and HF leaching) (see Fig. 5)

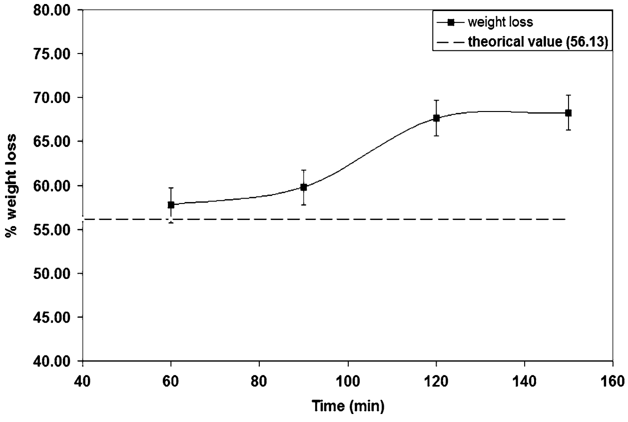


Fig. 3 Weight loss versus residence time

XRD data on powder samples confirm the SiC production (mostly β-SiC phase and a minor amount of α-SiC), as shown in Fig. 6; nevertheless the high background noise and the signals widening reveal the presence of an amorphous phase, probably due to the residual silica [36–38].

Thermogravimetric analysis (Fig. 7a–d) shows that a residual carbon content is still present in S1 and S2 samples (for residence time < 2 h) and is responsible for the mass loss registered at 700 °C in air; such a free carbon is actually absent in S3 and S4 samples ($t \geq 2$ h). These data are in accordance with the combustion data of the samples, which give no evidence of residual carbon for S3 and S4 samples (see Fig. 8). The thermograms also show the oxidation of the SiC at higher temperatures, with an evident mass gain (PM SiC = 40; PM SiO_2 = 60).

The total solid residue (that is the mixture of not reacted silica and ash from the char) and the residual silica are reported in Fig. 9 with respect to residence time: both the quantities (different from each other just for the ash content) linearly decrease with the time, at the same linear slope. As we see, the data related to S2 test (residence time of 90 min) are the closest ones to the theoretical values, while at higher residence time residual silica starts decreasing again.

SiC purity linearly increases at higher residence time, and a good agreement between experimental and theoretical purity value is once more achieved by S2 test (Fig. 10).

All these data seem to show that silica reactivity increases at higher residence times, even more than expected; nevertheless a greater SiO_2 consumption does not necessarily involve a higher SiC production. The conversion data (Fig. 11) show indeed that carbon reactivity is always very high (since carbon is the defective component and its conversion is almost 100%), while silica conversion linearly rises with residence time up to 100%, further than the theoretical value (87.47%); once again S2 test shows a conversion value very close to the expected value. But selectivity and yield (Figs. 12 and 13), calculated accounting for the stoichiometry of reaction (1) and reported either respect to carbon or silica, show a remarkable drop at higher residence time demonstrating that a higher conversion does not mean a higher SiC production.

A possible explanation is that a higher silica conversion (and a higher carbon conversion as well) corresponds to a major extension of reaction (2); nevertheless not all the produced SiO usefully reacts to synthesize SiC; accordingly, the yield passes through a maximum value (S2 test), then drops down when carbon content lowers.

The fluctuations of selectivity and yield, together with the higher silica conversion, seem to involve the participations of secondary reactions different from (2) and (3). As a matter of fact, once all the starting carbon is consumed, conversion, selectivity and yield are supposed to

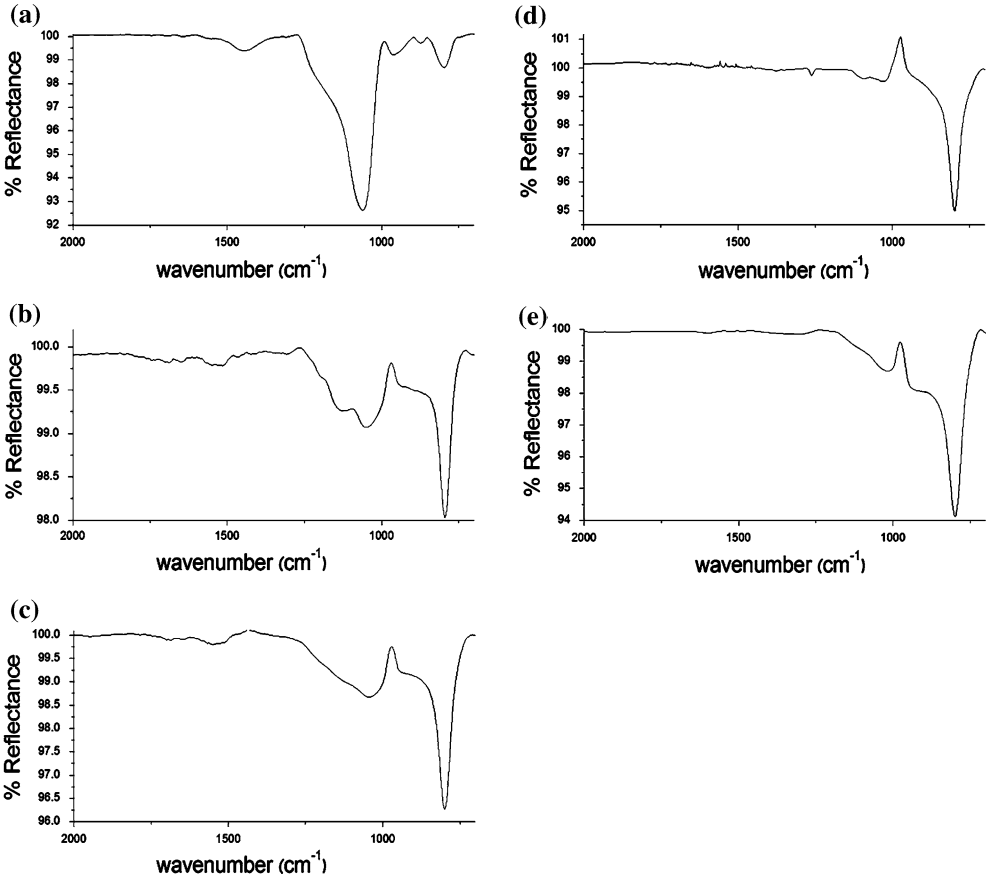


Fig. 4 FTIR spectra of products at different residence time: (**a**) starting mixture, (**b**) at 60 min, (**c**) at 90 min, (**d**) at 120 min, (**e**) at 180 min

get to a constant value: on the contrary, for residence time of 120 and 150 min (whose synthesis products were found to be carbon-free), silica conversion actually increases, while yield decreases and SiC production finally lowers. Likewise, the selectivity of both carbon and silica decreases, the latter reduction being more remarkable, due to the sum of two different contributions (decrease of SiC moles and increase of reacted silica).

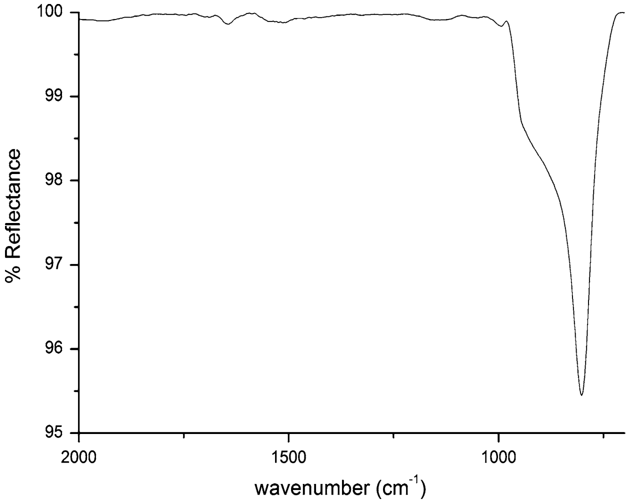


Fig. 5 FTIR spectra after purification

Since after 90 min of synthesis the residual carbon content is almost negligible, then the increase of silica conversion might be ascribed to a reactive path that could probably involve the consumption of the SiC already produced by means of oxidative reactions, such as:

$$\begin{aligned} &\mathrm{SiO_2(s) + CO(g) \Leftrightarrow SiO(g) + CO_2(g)} \\ &\Delta G_r^0 = 212.6\ \mathrm{kJ\,mol^{-1}}(T = 1,547\ ^\circ\mathrm{C}) \end{aligned} \tag{8}$$

$$\begin{aligned} &\mathrm{2SiO_2(s) + SiC(s) \Leftrightarrow 3SiO(g) + CO(g)} \\ &\Delta G_r^0 = 212.7\ \mathrm{kJ\,mol^{-1}}(T = 1,547\ ^\circ\mathrm{C}) \end{aligned} \tag{9}$$

$$\begin{aligned} &\mathrm{2CO_2(g) + SiC(s) \Leftrightarrow SiO(g) + 3CO(g)} \\ &\Delta G_r^0 = -212.5\ \mathrm{kJ\,mol^{-1}}(T = 1,547\ ^\circ\mathrm{C}) \end{aligned} \tag{10}$$

All these reactions are equilibrium reactions, then the followed direction will strongly depend upon the mass

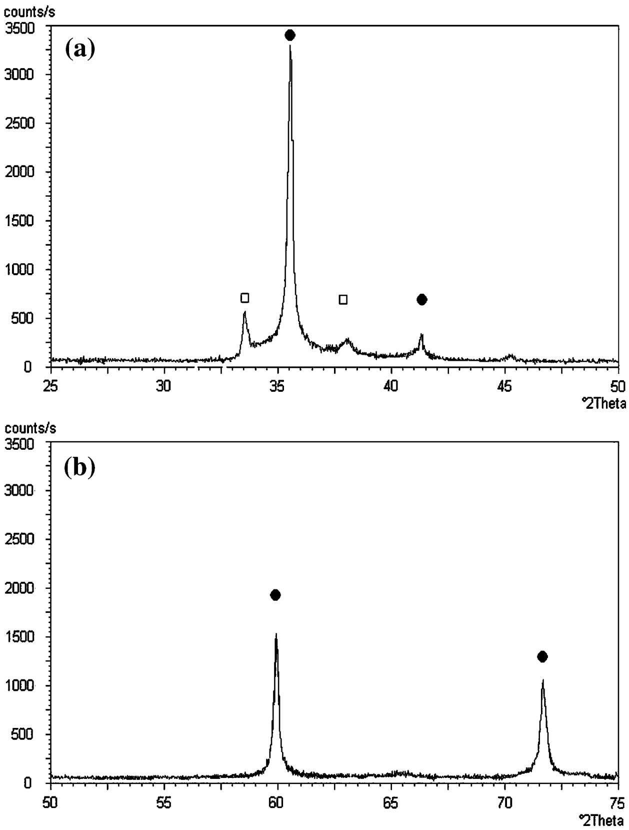


Fig. 6 XRD pattern of synthesis product at 1550 °C, Argon atmosphere, t = 120 min, ☐ α-SiC, ● β-SiC

effect at higher residence time. The corresponding increase of yield and selectivity should indicate a higher SiC production, probably due to gas-gas reactions [39, 40], such as:

$$\mathrm{SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g)} \tag{11}$$

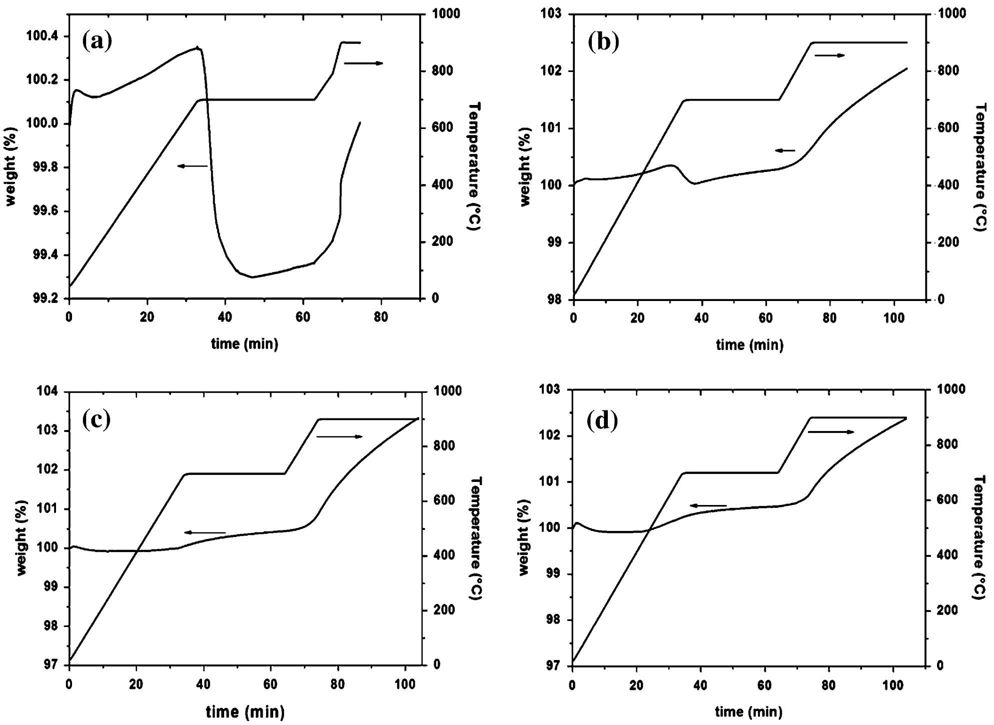
$$\mathrm{3SiO(g) + CO(g) \rightarrow 2SiO_2(s) + SiC(s)} \tag{12}$$

TEM analyses confirm the production of very thin spherically shaped SiC powders (Fig. 14) of 30–100 nm diameters, and sometimes, at higher residence time, the formation of fibres (Fig. 15a–c): the latter result matches the hypothesis of a gas-gas synthesis reaction, accounting for the reactive path above mentioned.

Conclusions

The synthesis of beta silicon carbide (β-SiC) powders was investigated, using as carbon source fine carbon-containing char from biomass gasification; such a precursor was isolated as solid residue of poplar steam gasification performed at 850 °C. The experimental surveys have been conducted at 1,550 °C by varying the residence times and the results have clearly confirmed the feasibility of char utilisation as a synthesis reagent. Maximum SiC yield was obtained with a residence time of 90 min, with a corresponding product purity of 80%; such a purity linearly

Fig. 7 Thermograms in air flowing for powders synthesized at 1550 °C for (**a**) 1 h; (**b**) 1.5 h; (**c**) 2 h; (**d**) 2.5 h



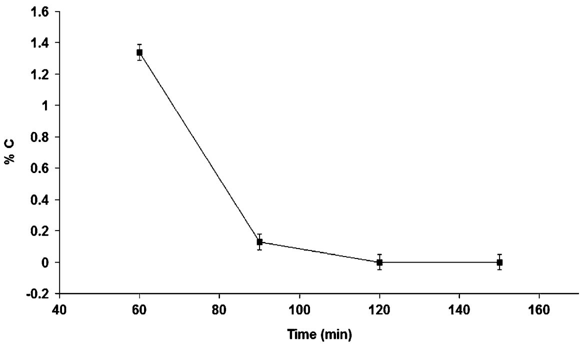


Fig. 8 Residual carbon content (%)

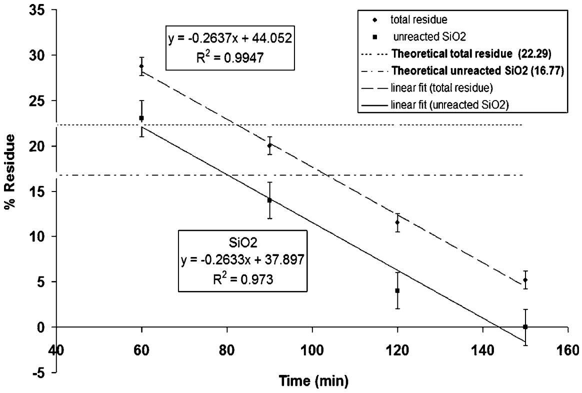


Fig. 9 Solid residue and SiO_2 residue (%)

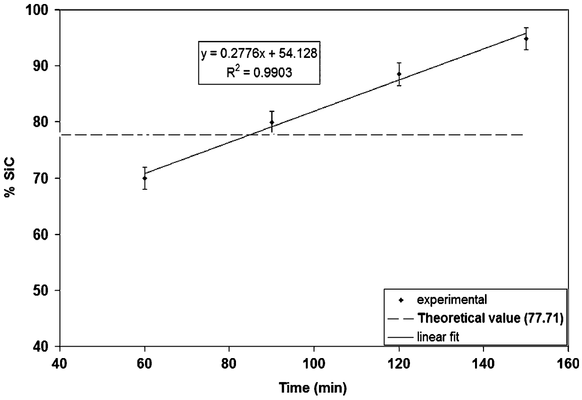


Fig. 10 SiC purity versus residence time (%)

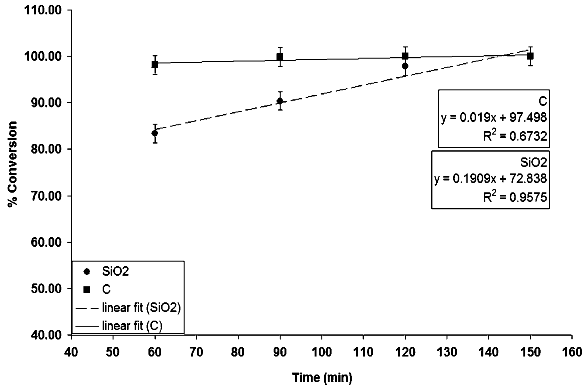


Fig. 11 Conversion versus residence time (%)

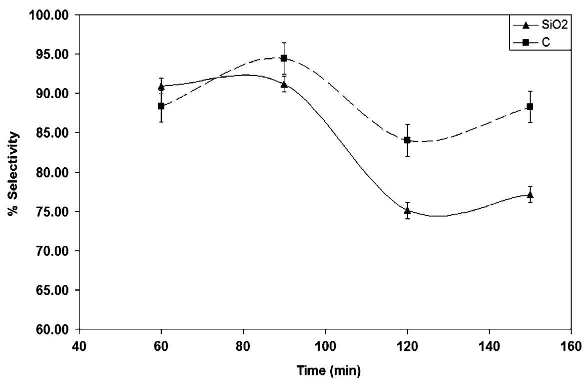


Fig. 12 Selectivity versus residence time (%)

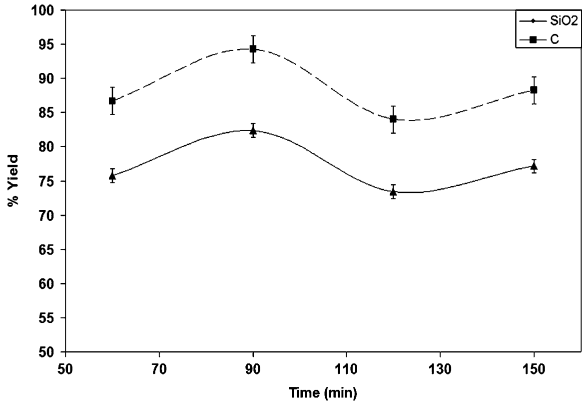


Fig. 13 Yield versus residence time (%)

increases with the residence time, but with lower yields. By the way it's still economically disputable if an in situ increase of purity, even if with yield reduction, would be better than a subsequent acidic purification of the product.

Furthermore the experimental surveys have shown that all the char contained carbon is suitable for the reaction, that is both the volatile and the inorganic fraction seem to join the reactive process.

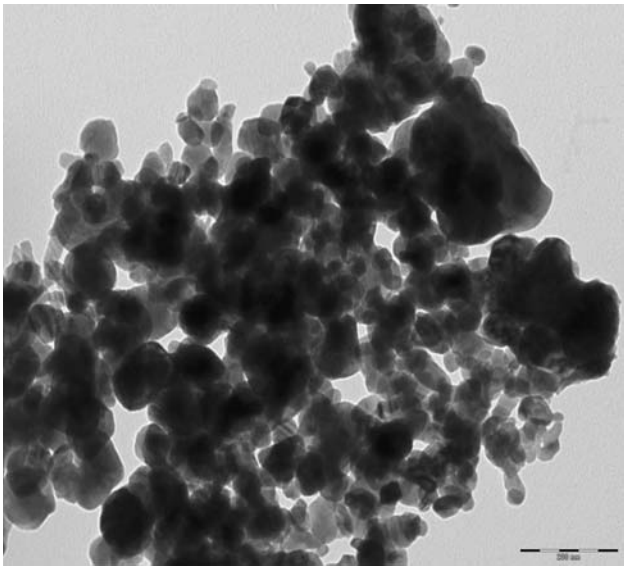


Fig. 14 TEM micrograph of SiC particles

TEM analyses indicate the production of nanometer-sized SiC powders, together with fibres production, probably due to gas-phase reactions of SiO and CO.

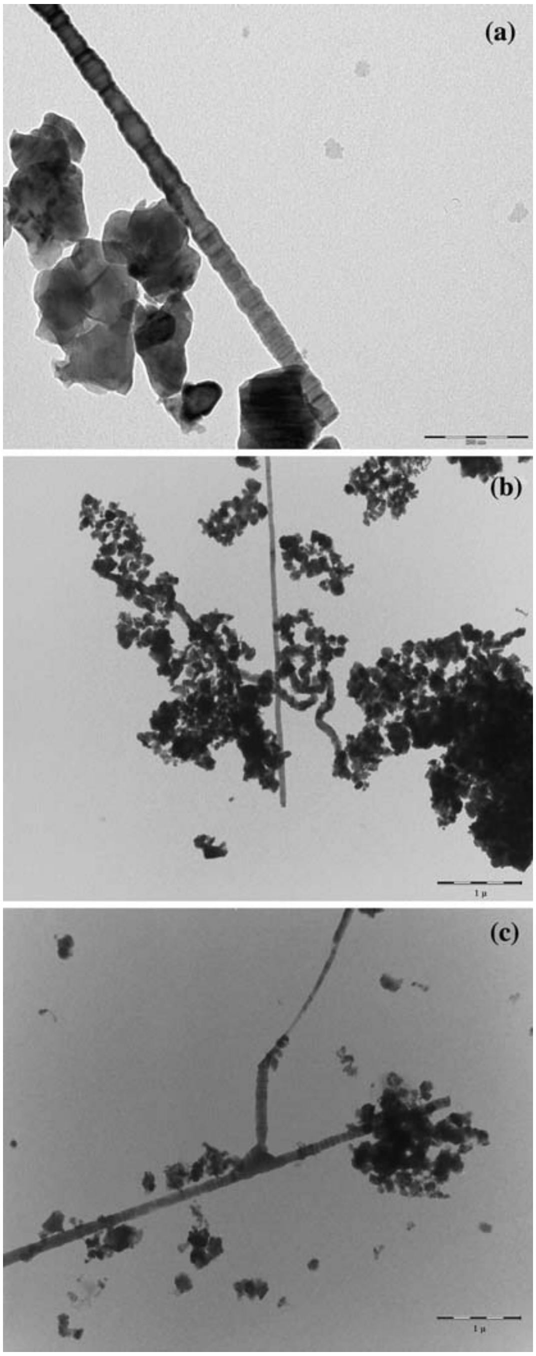


Fig. 15 TEM micrograph of SiC fibres (**a**), (**b**), (**c**)

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