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CO_2 and steam gasification of a grapefruit skin char[☆]

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Abstract

A kinetic study on the gasification of carbonised grapefruit (*Citrus Aurantium*) skin with CO_2 and with steam is presented. The chars from this agricultural waste show a comparatively high reactivity, which can be mostly attributed to the catalytic effect of the inorganic matter. The ash content of the carbonised substrate used in this work falls around 15% (db) potassium being the main metallic constituent. The reactivity for both, CO_2 and steam gasification, increases at increasing conversion and also does the reactivity per unit surface area, consistently with the aforementioned catalytic effect. Lowering the ash content of the char by acid washing leads to a decrease of reactivity thus confirming the catalytic activity of the inorganic matter present in the starting material. Saturation of this catalytic effect was not detected within the conversion range investigated covering in most cases up to 0.85–0.9. Apparent activation energy values within the range of 200–250 kJ/mol have been obtained for CO_2 gasification whereas the values obtained for steam gasification fall mostly between 130 and 170 kJ/mol. These values become comparable with the reported in the literature for other carbonaceous raw materials including chars from biomass residues and coals under chemical control conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Grapefruit skin chars; CO_2 and steam gasification; Reactivity

1. Introduction

Renewable energy sources have received increasing attention in the last three decades. Forest and agricultural wastes represent a significant contribution to the renewable resources inventory. Thermochemical conversion processes like pyrolysis and gasification provide a way of potential interest for energy and chemicals production and several R + D programs have been undertaken in developed countries to enhance the exploitation of biomass residues through those types of processes.

Gasification of carbonaceous raw materials is a flexible process which produces gases of variable composition and energy content depending on the gasification agent and the operating conditions. It may be oriented also to obtain activated carbon as a main product. Design and operation of gasifiers requires knowledge of the reactivity of the raw material to be processed with a given reacting gas. The most commonly used gasification agents are steam, air, CO_2 and mixtures of them.

The literature contains an extensive representation of works dealing with the reactivity of a variety of carbonaceous substrates under different approaches [1–8]. The nature, composition and structural characteristics of the substrate are recognized as determining factors regarding to the reactivity. The presence of some inorganic constituents plays in many cases a very important role due to catalytic effects. Sodium, potassium and calcium, which are commonly present in biomass, have shown a significant activity as gasification catalysts [3,9–11]. Both the porous structure and the intensity of the catalytic effects can undergo substantial variations, as gasification proceeds and this have to be considered to provide a satisfactory explanation of the reactivity versus conversion curves.

In this work, we study the CO_2 and steam gasification of carbonised grapefruit skin. Citrics represent one of the most important agricultural products in some world areas including developing countries. Transformation activities, as juices and jams production, leave considerable amounts of skin residues whose valorisation becomes advisable. Gasification can be a candidate process for that and thus it

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Table 1
Typical analyses of the char

Proximate analysis (wt%, db)	
Fixed carbon	71.8
Volatile matter	13.6
Ash	14.6
Elemental analysis (wt%, daf)	
C	89.9
H	1.9
N	1.7
O (by difference)	6.5
BET surface area (m^2/g)	≈ 10
D–R CO_2 surface area (m^2/g)	635

is of interest to learn about the behaviour of that residue in such process.

2. Experimental

The starting material for this work was the skin from peeling of grapefruit (*Citrus Aurantium*, var Macrocarpa) harvested from Pinar del Rio (Cuba). The skin was washed with water and air-dried at ambient temperature in the laboratory for about one month. A representative proximate analysis of the raw material on a dry basis (db) was 29.7% fixed carbon, 65.8% volatile matter and 4.5% ash content. A typical elemental analysis was 54.1% C, 6.9% H, 1.8% N and 37.2% O (by difference) on a dry ash-free (daf) basis.

The skin was grinded and the 1–1.6 mm fraction was carbonised at 700°C for 2 h in a conventional quartz tube furnace under N_2 atmosphere which was continuously passed at 150 ml(STP)/min. The resulting char gave the analyses reported in Table 1. It should be emphasised the relatively high ash content and the significant difference between the BET and the CO_2 (D–R) surface area values, the last substantially higher, indicative of a narrow microporous structure.

The gasification experiments were performed in an adapted thermogravimetric system (CI Electronics) described elsewhere [12]. An initial sample weight close to 10 mg was always used. In the CO_2 runs, a 60 ml(STP)/min flow of this gas was continuously passed whereas in the steam experiments we used N_2 at the same flow rate which was saturated of water vapour at temperatures of 15, 25, 60 and 80°C, thus corresponding to partial pressures of 1.7, 3.2, 19.9 and 47.4 kPa, respectively. All the experiments were carried out in isothermal regime and three different temperatures (725, 750 and 800°C) were checked. The reactivity was calculated from the weight loss curves as

$$r = \frac{1}{w}\frac{dw}{dt},$$

w being the remaining sample weight (in a daf basis) at each time.

ASTM procedures were used for proximate analyses and a 240 model Perkin–Elmer apparatus was used for elemental analyses. Surface area values of the starting char and partially gasified samples were determined from N_2 (77 K) and CO_2 (298 K) adsorption in a Quantachrome Autosorb-1 apparatus. XPS analyses of the char samples were obtained using a 5700C model Physical Electronics apparatus with Mg Kα radiation (1253.6 eV). Micrographs of the surface were also obtained, by means of a model JSM 840 JEOL Scanning Electron Microscope working at a 20 kV voltage.

3. Results and discussion

3.1. CO_2 gasification

Fig. 1 shows the reactivity curves obtained for CO_2 gasification of the char at 725, 750 and 800°C. The reactivity values increase as gasification proceeds, this increase being moderate up to about a 0.6 conversion but growing steeper beyond that value. This increasing reactivity can be explained in part as a result of the development of porosity usually accompanying gasification of char particles, leading to a higher surface area and consequently a higher concentration of carbon active sites per unit weight. Nevertheless, in spite of the relatively modest development of surface area (Table 2), this char shows reactivity values substantially higher than the encountered for other more or less similar carbon substrates [1,12–14] and comparable to the reported for catalysed gasification of active charcoals [15] and gas–coal chars [16]. These relatively high reactivity values and the steep increase within the high conversion range suggest the existence of an important catalytic effect due to the presence of some active species in the inorganic matter of the starting material. As reported in Table 1, the ash content of the char was a 14.6%, being potassium the major metallic constituent. The XPS spectrum of the char, shown in Fig. 2, confirms the presence of K and Ca, the former at a much higher concentration. The superficial K/C atomic ratio, as obtained from XPS, was 0.13, a fairly high value. The Ca/C atomic ratio was almost 10 times lower (0.015). As gasification proceeds the carbon material

Table 2
Normalized reactivity values per unit surface area (mg/m^2 min) for CO_2 gasification at 750°C

Conversion	BET surface area (m^2/g)	CO_2 surface area (m^2/g)	Normalized reactivity ($\times 10^3$)
0.35	405	665	15.7
0.48	475	710	16.6
0.61	460	575	22.6

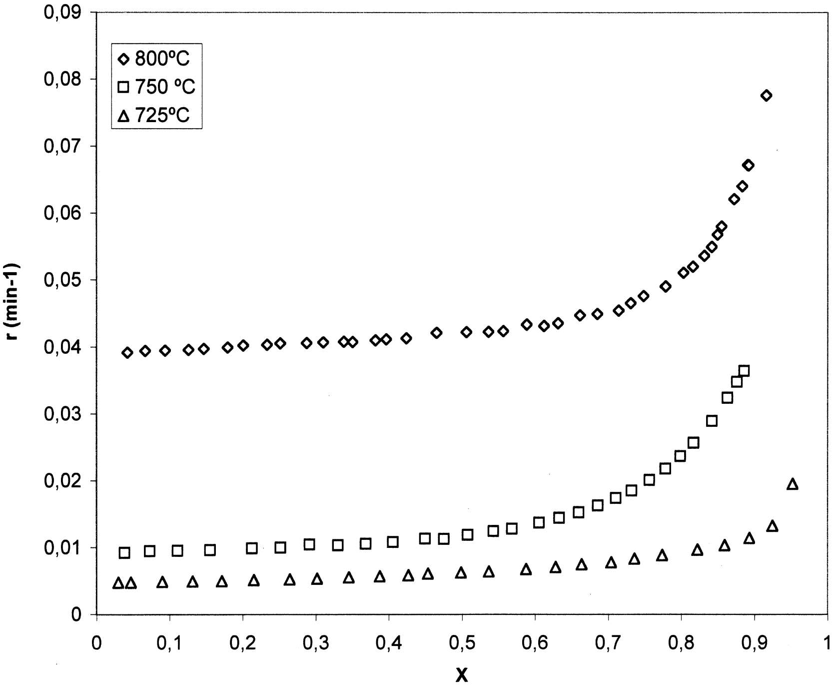

Fig. 1. Reactivity versus conversion curves for CO_2 gasification of the original char.

is consumed and the metal to carbon ratios increase so doing the intensity of the catalytic effect. The shape of the reactivity versus conversion curves of Fig. 1 indicates that saturation of catalytic activity does not occur even at conversion levels as high as 0.9 where the K/C ratio in the remaining solid must reach very high values taking into account that potassium losses through evaporation should not be important at the temperatures used in these experiments.

Table 2 shows the surface area of the active chars obtained from CO_2 partial gasification at different conversion values. The corresponding activation experiments were carried out at 750°C in the same conventional tube furnace system used for carbonisation. Using these surface area

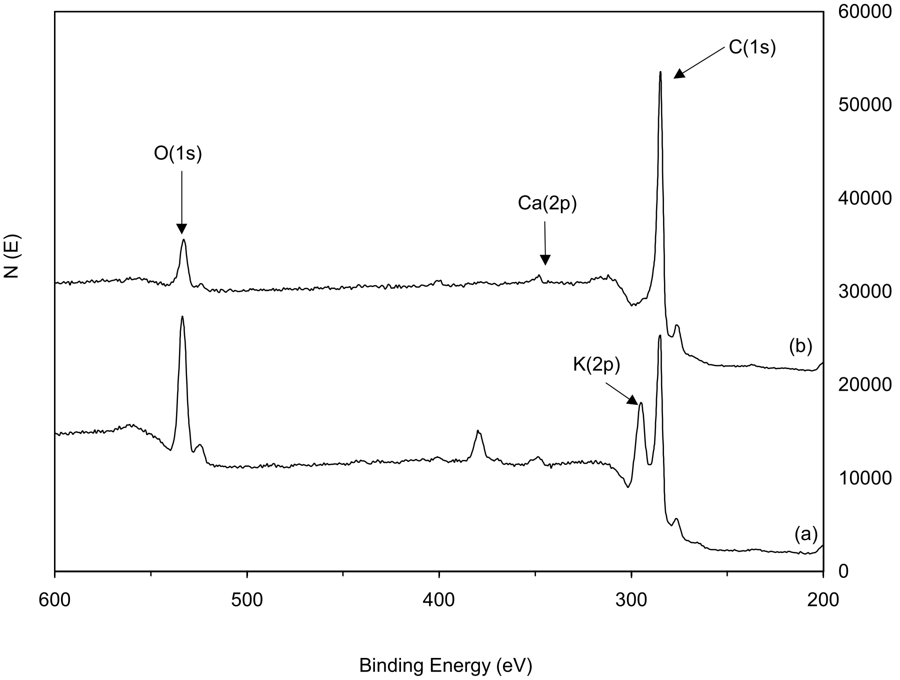

Fig. 2. XPS spectra of the (a) original and (b) washed chars.

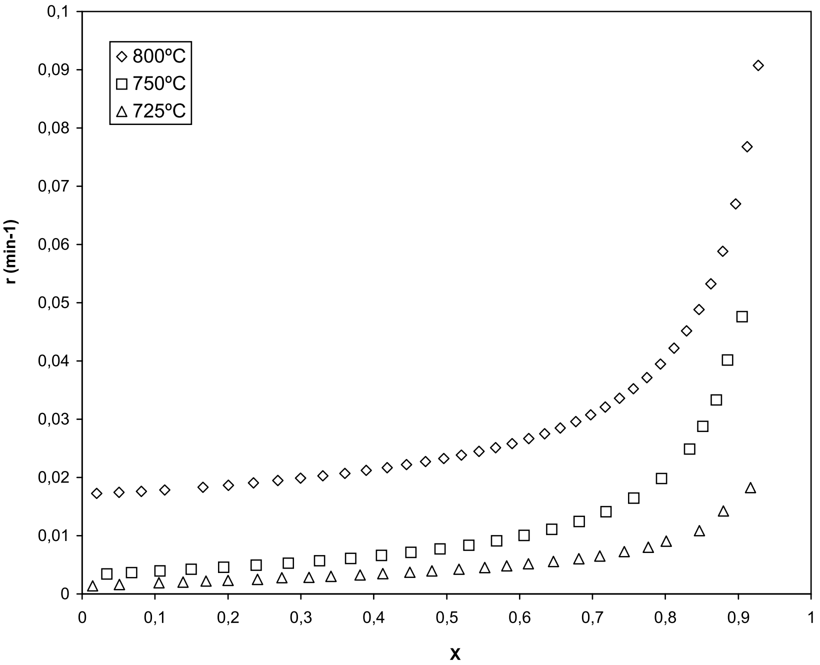

Fig. 3. Reactivity versus conversion curves for CO_2 gasification of the washed char.

values we have calculated the normalised reactivities per unit surface area, which are also reported in the table. The development of surface area upon gasification is fairly modest in comparison with the obtained from other biomass precursors [13,17,18], most probably due to the high ash content of our char. The CO_2 surface area values are in all the cases appreciably higher then the N_2 ones, which indicates that a great part of the surface area of the activated chars must correspond to narrow micropores or, most probably, that the inorganic matter partially blocks the entrance to the pores giving rise to restrictions to N_2 diffusion at the low temperature of the BET adsorption test. We have used the CO_2 surface area values as more representative of the available carbon surface area for gasification reaction. As can be seen, the reactivity values per unit surface area increase as conversion does, which is consistent with the existence of a catalytic effect contributing to the enhancement of specific rate of gasification.

To learn more about this catalytic effect, we prepared a char with a lower ash content (7.8%) simply by washing the original char with 0.5% (wt) H_2SO_4 aqueous solution followed by distilled water until negative sulphate analysis in the liquid. The reactivity versus conversion curves obtained for CO_2 gasification of this char are shown in Fig. 3. The reactivity values are now significantly lower than that obtained for the original char. CO_2-activation of the washed char at 750°C up to 0.4 conversion led to surface area values of $620\ m^2/g$ (BET) and $680\ m^2/g$ (CO_2), comparable to the obtained for the original char. The corresponding reactivity per unit CO_2 surface area was $9.7 \times 10^{-3}\ mg/m^2$ min, appreciably lower than the obtained for the original char at a comparable conversion value.

The XPS spectrum of the washed char is shown in Fig. 2 where it can be seen that the potassium peak has almost disappeared and only a small shoulder is observed. The superficial K/C atomic ratio has been strongly reduced up to 0.003. This reduction does not correspond by far with the decrease of the ash content of the char upon washing, suggesting that removal of inorganic matter affects essentially to the external surface of the particle and in a much lower amount to the internal or micropore surface, most probably due to diffusion limitations occurring upon washing as a consequence of the narrow microporosity of the char. That would explain the moderate decrease of reactivity as compared with what should be expected if the K/C ratio had lowered up to the above-mentioned value in the whole particle. The appearance of the external surface of the original and washed chars look quite different as can be seen from the SEM micrographs shown in Fig. 4. The second exhibits a more polished surface with some disseminated aggregates irregularly shaped which may correspond to inorganic matter whereas the surface of the former is homogeneously covered with small spherules also probably of inorganic matter.

As gasification progresses, the difference of reactivity between the original and washed chars becomes less important. So, at 800°C, the reactivity of the washed char is 53% of that of the original char at a 0.4 conversion whereas at 0.6 it is a 64% and a 77% at 0.8.

Table 3 shows the values of apparent activation energy obtained for CO_2 gasification of both the original and the washed char at different conversion levels. The values of the pre-exponential factor are also included. The activation energy values are indicative of a chemically controlled

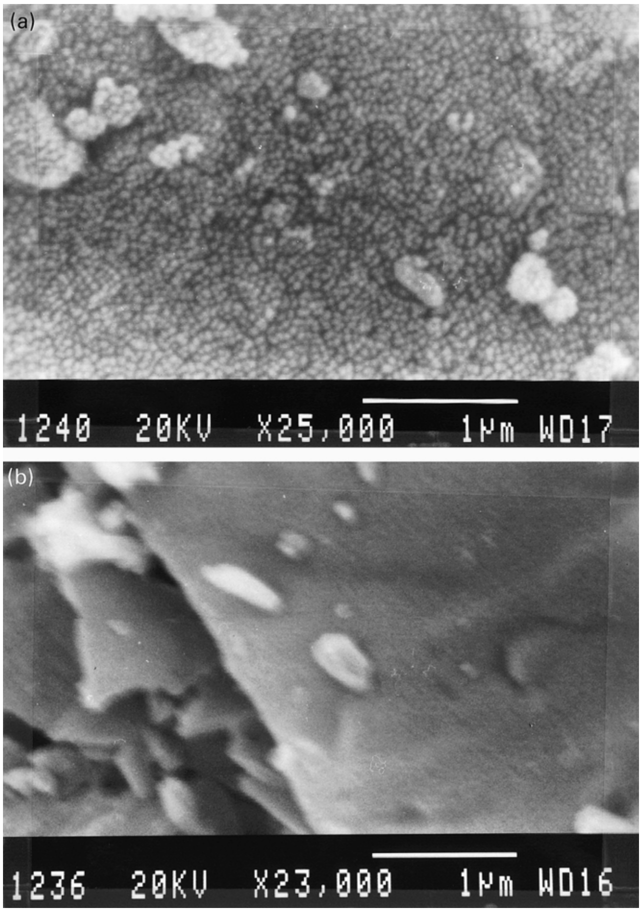

Fig. 4. SEM micrographs of the (a) original and (b) washed chars.

process and agree well with the reported for CO_2 gasification of different types of carbonaceous substrates [3,7,12,13,19–22]. There is a decrease of activation energy as conversion increases which although of not a high relative importance shows a monotonical trend. On the other hand, the energy values corresponding to the washed chars are somewhat lower than the obtained for the original char at the same conversion. These two observations are again consistent with the aforementioned catalytic effect. As can be seen from Table 3, the values of the pre-exponential factor vary in the same direction than those of activation energy. This trend has been frequently encountered in catalytic reactions and in particular in catalysed gas–carbon reactions [15,16,23,24], being the most common type of the so-called compensation effect of the kinetic parameters. Extrapolation of the Arrhenius plots corresponding to different conversion levels gave a value of the isokinetic temperature close to 1150 K in the case of the original char and 1180 K for the washed char. According to the interpretation given for some authors [15] that temperature would correspond to the one above which the catalyst would be ineffective. In our case it seems not unlikely that the catalytic effect ceases beyond about 1150–1200 K due to potassium loss through evaporation. Feistel et al. [24] obtained a higher value of the isokinetic temperature (about 1425 K) for potassium-catalysed gasification, although working with coals and using steam as gasification agent. Dhupe et al. [15] found also a close value of the isokinetic temperature for sodium-catalysed gasification of an active charcoal with CO_2.

Table 3
Apparent activation energy, E_a (kJ/mol) and pre-exponential factor, K_0 (min^{-1}) values for CO_2-gasification of the original and washed chars

Conversion	Original char		Washed char	
	E_a	K_0	E_a	K_0
0.2	249	4.42×10^{10}	248	2.30×10^{10}
0.4	236	1.15×10^{10}	220	1.03×10^{9}
0.6	219	1.80×10^{9}	196	8.90×10^{7}
0.8	197	2.70×10^{8}	176	1.50×10^{7}

3.2. Steam gasification

Fig. 5 shows the reactivity curves obtained for gasification of the original char with water vapour at a partial pressure of 3.2 kPa and at three different temperatures. For the shake of comparison we have included also the curve corresponding to the washed char at 800°C. The shape of the curves is similar to the ones obtained for CO_2 gasification except that now the increase of reactivity with conversion is more pronounced. Again, the reactivity of the washed char is smaller than the corresponding to the original char. As expected, the conclusion about the existence of a significant catalytic effect is thus valid as in the case of CO_2 gasification.

Values of apparent activation energy are reported in Table 4. These values are in good agreement with the reported in the literature for steam gasification of carbon substrates under chemical control conditions [4,25,26]. Opposite to CO_2 gasification, now the activation energy values increase somewhat at increasing conversion. This was accompanied by a parallel increase of the pre-exponential factor thus showing the common trend of E and K_0 varying in the same direction, although in this case both decrease as conversion increases, i.e. as increases the catalyst to carbon ratio. There are a few cases in the literature where such a trend has been reported in carbon gasification reactions [27].

Fig. 6 shows the reactivity curves obtained for the original char at 800°C and four different water vapour partial pressures. As can be seen, increasing that partial

Table 4
Value of apparent activation energy (kJ/mol) for steam gasification of the original char

Conversion	1.7 kPa	3.2 kPa
0.2	136	146
0.4	134	165
0.6	142	193
0.8	154	201

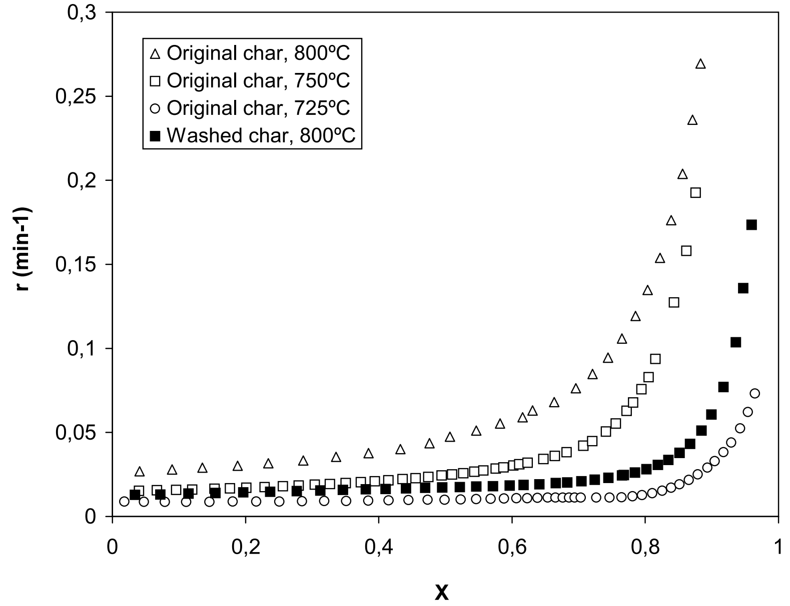

Fig. 5. Reactivity versus conversion curves for steam gasification at a partial pressure of 3.2 kPa.

pressure increases the reactivity. At low pressure a simple equation can be used to express the reactivity as a function of the concentration of the gasifying agent

$$r = kP^n$$

where k represents a kinetic constant, P is the partial pressure of the reacting gas (water vapour in this case) and n the reaction order with respect to it. Fitting the r and P values at constant conversion levels, we obtained the n values reported in Table 5. As can be seen, no significant variation of n with conversion is observed, except at higher conversion values where an increase of n takes place.

Table 5
Values of n for steam gasification of the original char

Conversion	n
0.1	0.57
0.2	0.56
0.3	0.55
0.4	0.53
0.5	0.53
0.6	0.53
0.7	0.61
0.8	0.73

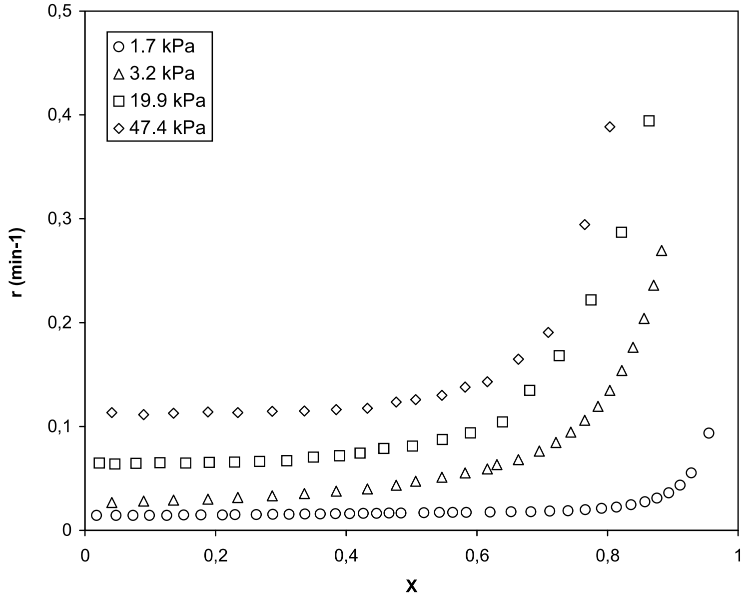

Fig. 6. Reactivity versus conversion curves for steam gasification of the original char at different partial pressures of water vapour.

A representative value of 0.5–0.6 can be taken for this parameter which is in good agreement with the reported by some other authors for steam gasification of coal chars [28].

4. Conclusion

Gasification can be an interesting way to process grapefruit skin and related wastes. Carbonizates from this residue show a relatively high reactivity, which will favour the application of this technique. This high reactivity can be mainly attributed to the catalytic effect of inorganic constituents, being potassium the most significant. Gasification should be oriented towards low to medium heating value gas for energy production at a relatively low scale. It has to be considered that complete gasification would leave about a 15% of the initial weight (db) of residue as ashes whose final disposal has to be regarded. The high potassium content of these ashes may facilitate some potential application, i.e. as fertilizer. Activated carbon manufacture through partial gasification would be less advisable due to the relatively low development of surface area and the predominantly narrow microporous structure of the resulting products even at high burn-off levels. These circumstances in addition to the high inorganic matter content would restrict the commercial value and the potential uses of these activated carbons.

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