

Influence of temperature and heating rate on the fixed bed pyrolysis of meat and bone meal

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Received 6 February 2006; received in revised form 11 April 2006; accepted 14 April 2006

Abstract

This work is focused on the study of meat and bone meal pyrolysis in a fixed bed reactor, analysing the influence of the final pyrolysis temperature and heating rate on the product (char, tar and gas) distribution and composition and the char characterization. Two sets of experiments have been performed at different final pyrolysis temperatures between 300 and 900 °C and heating rates from 2 to 14 °C/min. From the results obtained it is observed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate, except on the temperature profiles. The analysis of pyrolysis product distribution shows that the major products obtained were tar and char at any temperature or heating rate. Most of the decomposition takes place at temperatures lower than 500 °C, and no more significant decomposition is produced above 750 °C. The chars obtained present a low specific surface area, less than 45 m²/g. The tar obtained is mainly composed of more than 60% nitrogenated aliphatic compounds (such as nitriles, amides and cyclic compounds), 15% aliphatic hydrocarbons (such as alkanes and alkenes), 10% oxygenated aliphatic compounds (mostly carboxylic acids) and about 8% oxygenated aromatic compounds (mainly phenolics).

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Keywords: Biomass conversion; Pyrolysis; Meat and bone meal

1. Introduction

Meat and bone meal (MBM) is generated in substantial quantities and is no longer allowed by law to be used as animal feed. The reason is that bovine, ovine and caprine MBM and carcass are considered specific risk material (SRM) which could be responsible for Bovine Spongiform Encephalopathy (BSE). The prion that causes the infection can be destroyed by combustion at 850 °C for at least 2 s, or at 3 bar and 133 °C for at least 20 min.

One solution adopted for the disposal of MBM is landfill. However, the prion is not destroyed and previous treatment is required before the disposal. Another solution is destruction by combustion or incineration although the latter process is today a controversial one because of the fly ash emanating from incineration plants and the production of furans and dioxins. Nevertheless, it has been demonstrated that the amount of furans and dioxins produced by MBM incineration are much

lower than that of sewage sludge or refuse derived fuel incineration [1]. Moreover, the BSE risk associated with fly ash is negligible [2].

On the other hand, there are various problems arising from the use of combustors such as the agglomeration of ashes at high temperature [3] and the necessity of feeding the MBM with other material such as peat [4] or coal [5] to ensure its effective combustion.

Other authors have demonstrated the potential use of the ash obtained in combustion and gasification as an adsorbent material to remove lead from aqueous effluent [6] and as a low cost pure phosphate source with no heavy metal content (Ni, Cr or Cd) [7].

Other thermal treatments, such as gasification or pyrolysis, could be interesting alternatives for making effective use of MBM. This work is specifically focussed on the study of pyrolysis as a possible thermal treatment of MBM to transform it into products with higher energetic values. A few pyrolysis studies have already appeared in the literature. For example, it has been found that the kinetics of the MBM pyrolysis reaction can be described by different initial fractions which decompose independently following a first [8] or second order [9] set of

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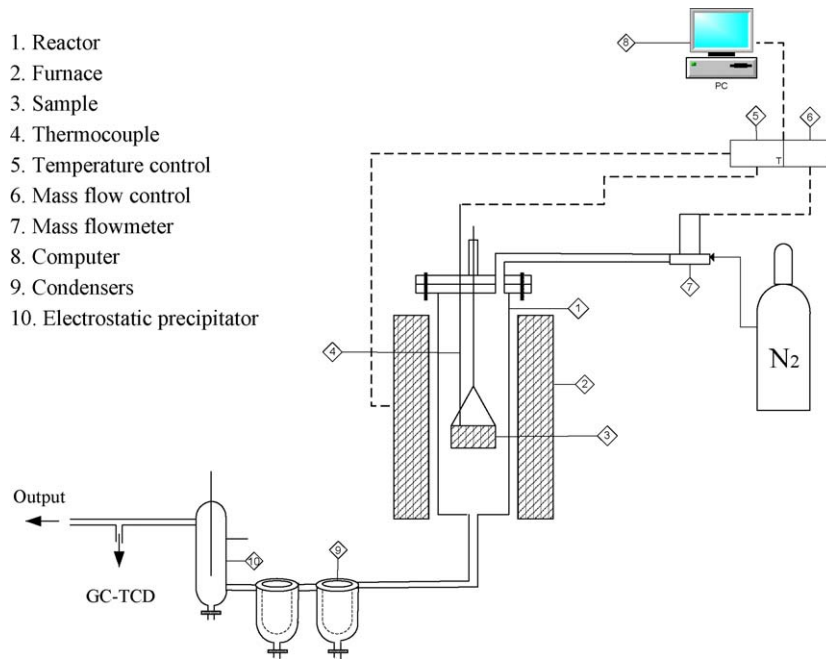


Fig. 1. Experimental system used.

reactions. Chaala and Roy have studied vacuum pyrolysis treatment at 500 °C and 15 °C/min [10], their results revealing the advantages of this process for treating MBM because it generates valuable products which can be used in other processes: combustible gas (LHV: 12.9 MJ/kg), high calorific value oil (HHV: 34.2 MJ/kg), a solid residue rich in minerals and an aqueous phase rich in organics. Apart from this work, however, there are no data about the product distribution and composition from the pyrolysis of MBM at different operating conditions. Thus, the objective of this work is to evaluate the pyrolysis process of MBM in a fixed bed reactor by analysing the influence of the final pyrolysis temperature and heating rate on the product distribution and composition (char, tar and gas). Since char is the material that could be subsequently gasified, the influence of temperature and heating rate on its surface area was also determined. This information is of great interest in order to evaluate the pyrolysis of MBM as a thermal process in itself and as the first step in more complex processes such as gasification, combustion, or integrated systems.

2. Experimental

The pyrolysis runs were performed in a bench scale plant, shown in Fig. 1, consisting of a fixed bed reactor of 90 mm in diameter and 320 mm in length, discontinuous for the solid feed. The reactor is inside a tubular electric furnace of 325 mm in length, 355 mm in external diameter and 120 mm in internal diameter, connected to a temperature and heating control system. Computer software provides a continuous record of carrier gas flowrate, time, temperature of the furnace and temperature of up to six thermocouples placed in the sample.

A steel basket with a radius of 28.3 mm and height of 41 mm containing a sample weight of 30 g was placed in the reactor

prior to the experiment and hung at a depth of between 201 and 245 mm from the top. This basket has two mesh screens, the external one having a diameter of 1000 μm and the internal one of 40 μm . The temperature profiles inside the sample were monitored placing the thermocouples in eight different positions, at two radii: 0 and 27 mm, and four heights: 1, 8, 15 and 22 mm from the bottom of the basket. Fig. 2 shows a scheme of the basket and the position of the thermocouples.

Once the reactor is closed, a nitrogen flow of 13 cm³NTP/s (NTP: normal temperature and pressure, 0 °C and 1 atm) is set by means of a mass flow controller. After 30 min under nitrogen flow, when the air is purged from the reactor, heating of the sample starts at the selected heating rate from 30 °C until the final pyrolysis temperature is reached. The temperature of the reactor is then kept constant for 90 min to make sure that the pyrolysis process is complete.

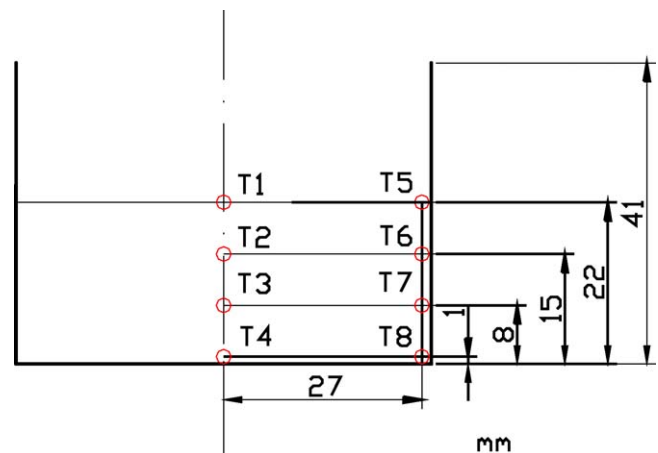


Fig. 2. Scheme of basket and position of thermocouples inside the sample.

The exit gas passes through a tar condensation system which consists of two glass condenser vessels cooled with a mixture of ice and water and an electrostatic precipitator. Two different methods for collecting the gas were used. In the first, the whole gas produced is collected in Tedlar bags and analysed. In order to follow the evolution of the gas composition with time for each experiment, a second method is used, consisting of taking gas samples every 5 min and analysing them. The clean gas is analyzed by GC-TCD, in a system equipped with a Porapak N column and a Molecular Sieve. The compounds analyzed are H_2 , N_2 , CH_4 , CO , CO_2 , C_2H_6 , C_2H_4 , C_2H_2 and H_2S . Heavier compounds were not detected in the experimental conditions used in this study. Once the experiment is finished and the system is cooled down to room temperature, the char is removed from the basket and weighed. The tar collected by the tar condenser system is also weighed and subsequently extracted with 2-propanol. The diluted sample of tar is analyzed by GC-MS and GC-FID in order to identify and quantify the compounds present. The specific surface area of the char was measured by MICROMERITICS equipment, the Pulse ChemiSorb 2700 model using nitrogen (BET method).

The material used in the experiments was meat and bone meal in powder form with a particle size smaller than 3 mm. The initial sample mass was 30 g in all the experiments performed. The ultimate (dry basis) and proximate analyses of the sample used in the pyrolysis experiments are shown in Table 1. The lower heating value (LHV) of the meat and bone meal used was 19,600 kJ/kg (as received).

Before studying the pyrolysis process, some experiments to obtain the temperature profiles and the gas residence time in the reactor were necessary. To obtain the temperature profiles, K type thermocouples of 1/16" were placed at several points of the reactor to measure the temperature at different depths ($z = 80$,

Table 1

Ultimate (dry basis) and proximate analysis for the meat and bone meal under study

Element	(wt.%)	Component	(wt.%)
C	45.92	Moisture	1.38
H	6.35	Ash	17.48
N	8.89	Volatile matter	71.45
O ^a	38.40	Fixed carbon	9.69
S	0.44		

^a Calculated by difference.

160, 200, 240 mm), radii ($r = 0, 20, 40$ mm) and angles ($\theta = 0^\circ, 90^\circ, 180^\circ, 270^\circ$); z measures the distance to the top of the reactor and θ is the angular cylindrical coordinate. The location of the nitrogen inlet corresponds to $\theta = 90^\circ$ and from here the remaining positions are established in an anticlockwise direction. A scheme of the position of the thermocouples is shown in Fig. 3. The heating rate was $10^\circ\text{C}/\text{min}$ for all these experiments. To calculate the gas residence time, isothermal experiments at different temperatures (300, 450, 600, 750 and 900°C) were carried out. The gas residence time is required to correct the gas sampling time for the gas evolution study.

Once the best place to locate the sample in the reactor without noticeable temperature profiles was selected, $z = 245$ mm, two sets of experiments were performed. The first set was carried out at a constant heating rate ($8^\circ\text{C}/\text{min}$) and different final pyrolysis temperatures (300, 350, 400, 450, 500, 550, 600, 750, 825 and 900°C) and the second set at different heating rates (2, 8 and $14^\circ\text{C}/\text{min}$) and different final pyrolysis temperatures (300, 450 and 600°C). The results analysed in both sets were temperature profiles inside the sample, product distribution and composition (char, tar and gas) and characterization of the char (specific surface area and scanning electron microscopy (SEM) images).

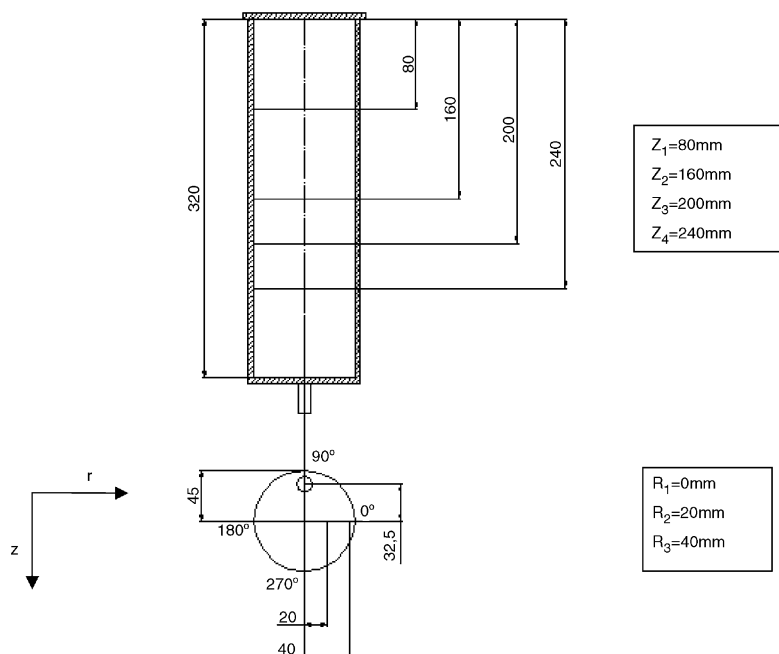


Fig. 3. Scheme of the reactor and position of thermocouples to determine temperature profiles.

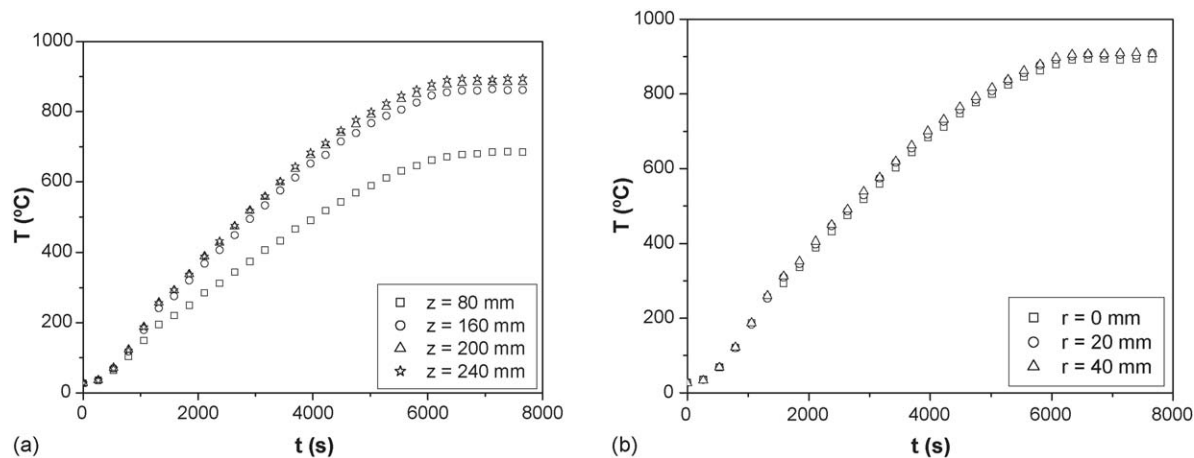


Fig. 4. Temperature profiles inside the reactor: (a) longitudinal profiles at radius = 0 mm; (b) radial profiles at 270° and 240 mm.

Most of the runs performed were repeated in order to test the reproducibility of the experimental system and procedure. The coefficient of variation of the percentage in weight of the different products obtained was: 3% for char, 5% for tar and 10% for gas.

3. Results and discussion

3.1. Temperature profiles and gas residence time in the reactor

Experiments were performed prior to the pyrolysis runs in order to minimize the effect of the temperature profiles inside the reactor.

It was possible to minimise the temperature gradients by hanging the sample basket at 245 mm from the top of the reactor, as can be seen in Fig. 4a for a radius = 0 mm. For other radii the results are similar. At this position the radial and angular temperature profiles are flat, see Fig. 4b as example.

The gas residence time for each temperature is shown in Table 2. As has been mentioned, these values are necessary in order to correct the gas sampling time for the study of the gas evolution during the experiment.

3.2. Temperature profiles inside the sample

Temperature profiles inside the sample were studied in order to gain a better understanding of the pyrolysis process. The results obtained in these experiments revealed the existence of longitudinal, radial and angular temperature profiles inside the sample. The existence of the angular profiles could be due to the

fact that the nitrogen entry is placed at the top of the reactor and at 32.5 mm from its centre. As regards the radial profiles, the temperature increases with the radius. This is logical, since the heating flow from the furnace is lateral. For these reasons, the results presented in Fig. 5 correspond to the longitudinal temperature profiles at the centre of the sample (radius 0). In this figure, T_{control} is the temperature measured by a thermocouple placed near the sample and which is used to control the heating rate of the electric oven. As can be observed, temperature profiles are constant at 2 °C/min (Fig. 5a), the bottom part of the sample being slightly hotter than the rest at any temperature. On the other hand, a profile inversion is observed between 350 and 400 °C at heating rates of 8 and 14 °C/min, Fig. 5b and c respectively. At the beginning of the run and up to 350–400 °C, the temperature inside the sample is significantly lower than T_{control} , the top of the sample being the hottest part. However, after the inversion, the temperature inside the sample is much closer to T_{control} although the bottom part is slightly hotter and the temperature differences with T_{control} are around 10 °C for the experiment at 14 °C/min. The temperature profiles are much higher at 8 and 14 °C/min than 2 °C/min.

This phenomenon of temperature inversion has also been observed in studies of the pyrolysis of sawdust and cellulose [11]. According to some works performed with wood particles [12], conduction could be considered as the main mechanism of heat transmission inside a bed of solids, and when the sample has a low thermal conductivity, high temperature profiles are created inside the particle. As can be observed in Fig. 5c, the temperature differences with T_{control} before the inversion are around 120 °C for the experiment at 14 °C/min. Furthermore, it must be considered that pyrolysis reactions are mainly endothermic and, as was observed in pyrolysis experiments carried out in a thermobalance [9], most decomposition reactions take place between 200 and 450 °C. Thus, when MBM decomposition is occurring, the heat transfer rate into the bed could be slower than the heat rate consumption due to the pyrolysis reactions. When pyrolysis is almost complete, energy is only used to heat up the sample, and the heat transfer rate is sufficient to avoid the temperature gap between T_{control} and the sample. On the

Table 2
Gas residence time inside the reactor at different temperatures

T (°C)	t (min)	T (°C)	t (min)
300	4.60	750	3.27
450	4.40	900	3.31
600	4.06		

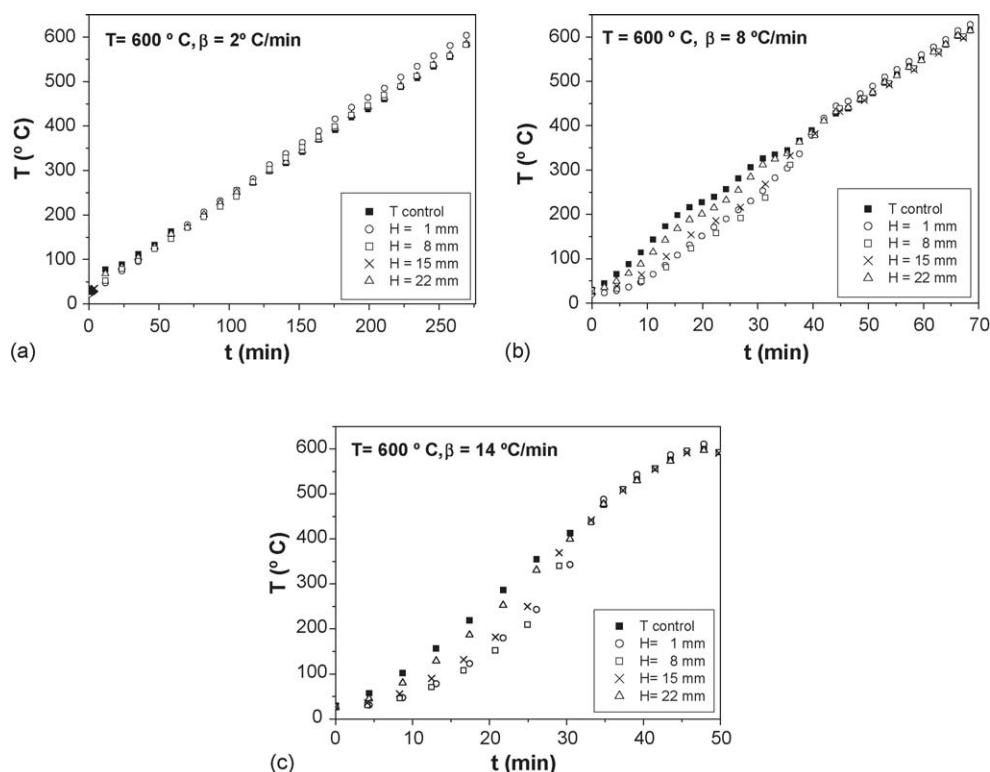


Fig. 5. Temperature profiles at centre of the sample for experiments at 600 °C and different heating rates: (a) 2 °C/min; (b) 8 °C/min; (c) 14 °C/min.

other hand, when the heating rate is low (2 °C/min), the heating of the sample is homogeneous because the decomposition is slower.

3.3. Effect of the final pyrolysis temperature on the pyrolysis process

In order to evaluate the effect of the final pyrolysis temperature on the pyrolysis process a wide range of temperatures (300–900 °C) was tested at 8 °C/min.

3.3.1. Product distribution

The products obtained from pyrolysis are gas, tar and char. As can be observed in Fig. 6, the main products in the pyrolysis process at any temperature studied are tar and char. The gas yield increases with the temperature up to approximately 825 °C, up to about 20% of the MBM in weight at 900 °C. The char yield decreases with temperature and the tar yield increases until 450 °C, then its value remains practically constant (the variation observed in Fig. 6 is due to the coefficient of variation of the tar measurement, which is 5%).

3.3.2. Gas composition

The compounds analysed in the gas product were: CO₂, CO, CH₄, H₂, C₂H₄, C₂H₆, C₂H₂ and H₂S. Fig. 7 displays the volume percentage of each compound in the gas product (in a nitrogen free basis) with the final pyrolysis temperature.

As can be observed in Fig. 7a, under all operating conditions the main compound is CO₂, but its percentage volume decreases

sharply as the temperature rises. From 500 °C the second main compound is H₂, which rises slightly until 450 °C, increases at a faster rate until 600 °C while from 600 to 900 °C its percentage volume increases more slowly. The production of CO rises with the final pyrolysis temperature, while CH₄ has a maximum at 500 °C.

The influence of temperature on the production of C₂H₆, C₂H₄, C₂H₂ and H₂S is plotted in Fig. 7b. It is observed that the organic compounds have a maximum at different tempera-

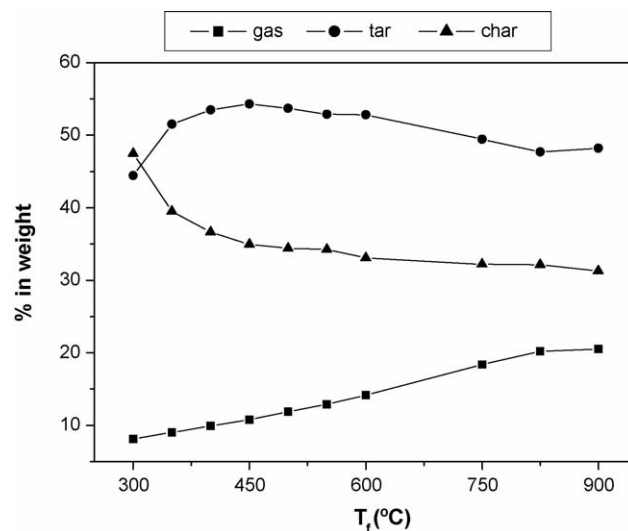


Fig. 6. Evolution of product distribution with final pyrolysis temperature for experiments at 8 °C/min.

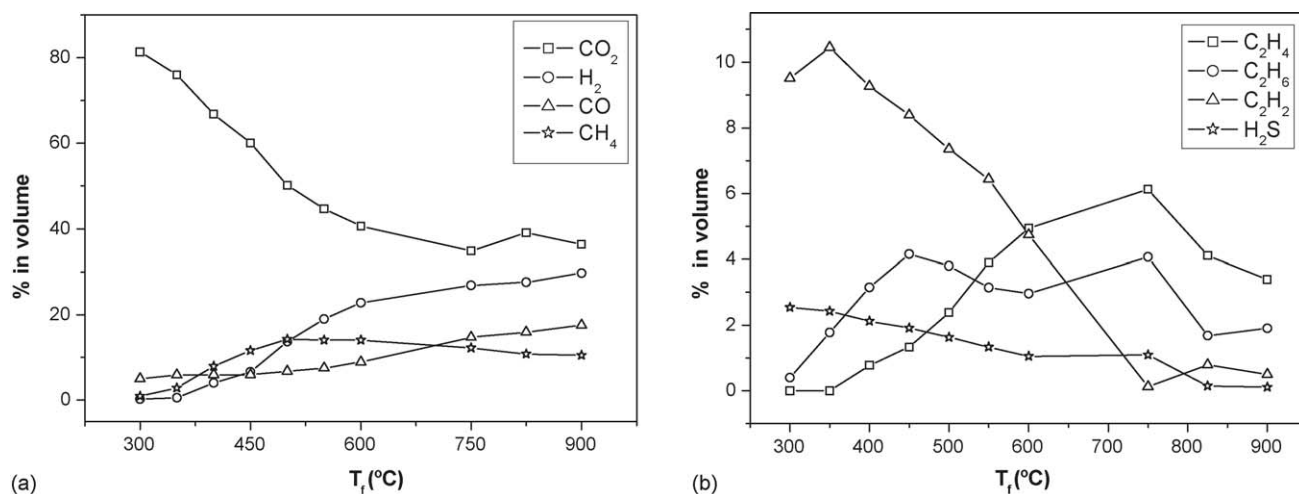


Fig. 7. Evolution of gas composition with final pyrolysis temperature for experiments at 8 °C/min: (a) CO_2 , CO , H_2 and CH_4 ; (b) C_2H_6 , C_2H_4 , C_2H_2 and H_2S .

tures, for example, C_2H_6 at 450 °C, C_2H_4 at 750 °C and C_2H_2 at 400 °C. H_2S decreases with the temperature.

At the beginning of the decomposition (until around 300 °C) CO_2 and CO are mostly produced. This could be due to the fact that the evaporation of low molecular weight compounds takes place at low temperatures, as well as decomposition reactions with scission of C–C bonds. This fact was also observed in the decomposition of sewage sludge by Chen and Jeyaseelan [13]. On the other hand, high temperatures favour the production of H_2 and CH_4 . Similar results are obtained in the pyrolysis of other waste materials, such as tyres [14,15] or hardware components [16]. According to Dai et al. as temperature rises the heavier hydrocarbons are cracked producing lighter ones, methane and hydrogen [15].

It can also be observed that the higher the final pyrolysis temperature, the less CO_2 is produced, while CO increases. According to Díez et al. it could be a consequence of secondary reactions taking place during the pyrolysis, in which CO is formed from reactions in the gas phase between CO_2 and hydrocarbons or from other cracking reactions [14].

The lower heating value of the gas increases significantly until 500 °C, remains practically constant from 500 to 600 °C, and decreases to around 12,500 kJ/m³NTP at temperatures higher than 600 °C (Fig. 8). This is probably explained by the fact that most of the MBM decomposition occurs between 200 and 450 °C.

The cold gas efficiency was defined as the ratio of the average low heating value of the gas per the low heating value of the sample (Eq. (1)).

$$\eta = \frac{(V_g \times \text{LHV})/m_{\text{MBM}}}{\text{LHV}_{\text{MBM}}} \times 100 \quad (1)$$

where V_g is the gas volume (m³NTP), LHV the average lower heating value of the gas produced (kJ/m³NTP), m_{MBM} is the weight of the sample (kg), LHV_{MBM} is the lower heating value of the meat and bone meal (kJ/kg).

The cold gas efficiency increases with temperature, considerably at low pyrolysis temperatures and slightly from 600 °C. The maximum value obtained is about 12% at 900 °C. This

value might be sufficient to sustain the pyrolysis process itself.

3.3.3. Tar composition

Tar is the main product obtained in the experimental conditions tested. In Fig. 9 it can be observed that 50% of the tar is produced below 300 °C and it is almost completely depleted at

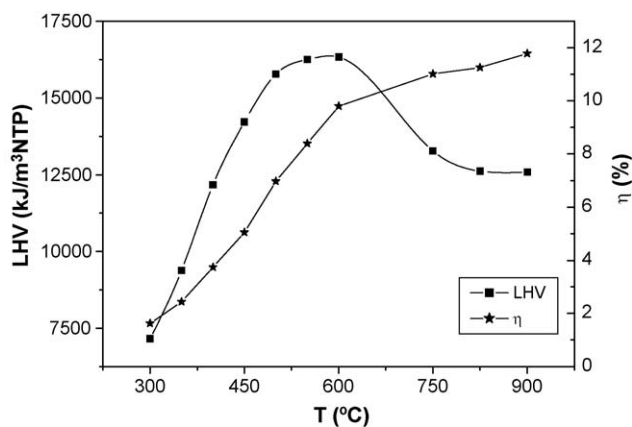


Fig. 8. Lower heating value and cold gas efficiency vs. final pyrolysis temperature for experiments at 8 °C/min.

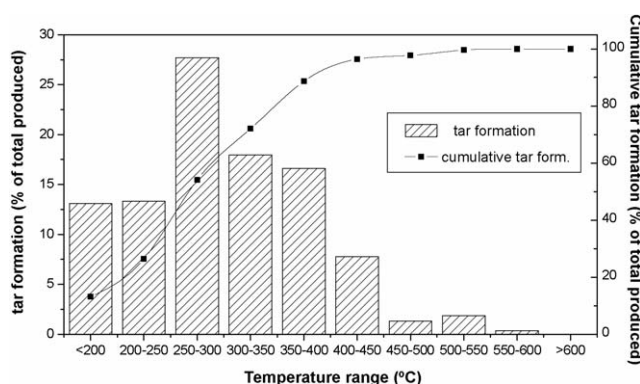


Fig. 9. Tar production and cumulative tar production vs. temperature.

Table 3

Tar compound classification

Aliphatic hydrocarbons	Alkanes Alkenes Cyclic hydrocarbons
Aromatic hydrocarbons	Monoaromatic hydrocarbons Aromatic methyl derivatives Polyaromatic hydrocarbons
Oxygenated aliphatic hydrocarbons	Ketones Aldehydes Carboxylic compounds Anhydrides Ethers Alcohols
Oxygenated Aromatics	Phenols Others
Nitrogenated aliphatics	Nitriles Amides Amines Cyclic compounds Others
Nitrogenated aromatics	Aromatic nitriles Heterocyclic nitrogenated aromatics

450 °C. Approximately 30% of the total tar produced is depleted in the 250–300 °C range.

Around 120 compounds have been detected in the tar obtained, most of them being present in very low percentages. In order to facilitate the study of the evolution of the tar composition with the temperature, the compounds detected have been grouped according to their chemical nature (see Table 3). The tar composition obtained at each temperature range considered is shown in Fig. 10. It can be observed that nitrogenated aliphatic compounds are the most significant group in all the temperature ranges, reaching about 83% of the tar produced in the 500–550 °C temperature range. Between 300 and 550 °C aliphatic hydrocarbons represent 20–30% of the tar produced, whereas each of the other groups roughly represent less than 10% of the tar produced at each temperature range considered. The tar obtained below 200 °C contains 21% of oxygenated aliphatic compounds, mainly carboxylic acids, but at higher temperatures the quantity is less significant.

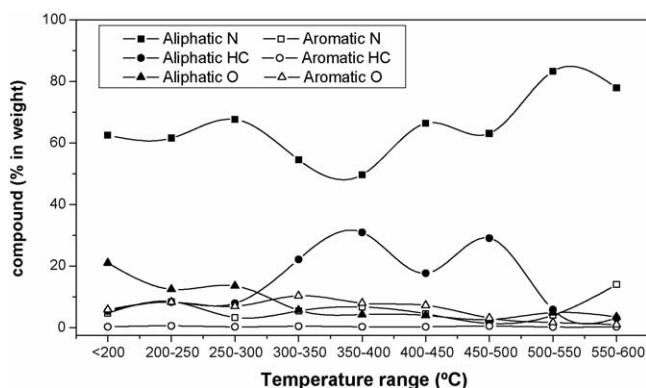


Fig. 10. Composition of tar produced at different temperatures.

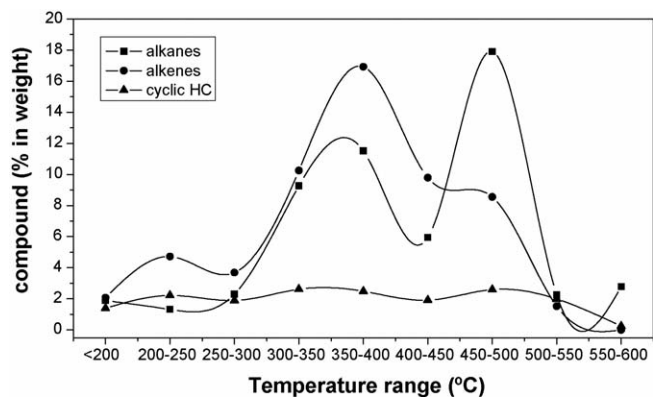


Fig. 11. Evolution of aliphatic hydrocarbons (as a percentage of the total tar produced at each temperature) with temperature.

Aromatic hydrocarbons represent less than 1% of the tar produced at each temperature range. And nitrogenated aromatic compounds are not present in the tar produced in significant quantities up to 550–600 °C. In this temperature range they represent 14% of the tar produced (quinoline being the principal compound detected) which, as Fig. 9 shows, is about 1% of the total tar produced. Oxygenated aromatics increase with temperature up to 300–350 °C, in which range they represent 10% of the tar produced. The main compounds detected are phenol, 4-methyl phenol and 2,4-dimethyl phenol.

The evolution with temperature of aliphatic hydrocarbons, nitrogenated aliphatic and oxygenated aliphatic compounds (as a percentage of the total tar produced at each temperature) are shown in Figs. 11–13.

At temperatures between 200 and 450 °C alkenes are the most important aliphatic hydrocarbons (Fig. 11), whereas alkanes are mostly produced between 450 and 500 °C. Cyclic hydrocarbon composition is around 2.5% weight at all temperatures.

Nitrogenated aliphatic compounds are the most important at any temperature range. In Fig. 12 it can be observed that at low temperatures, nitrogenated cyclic compounds and amines represent about 65% of the tar, whereas at 550–600 °C the main groups present are cyclic compounds and nitriles.

Oxygenated aliphatic compounds are mainly present at low temperatures making up around 20% of the tar produced below

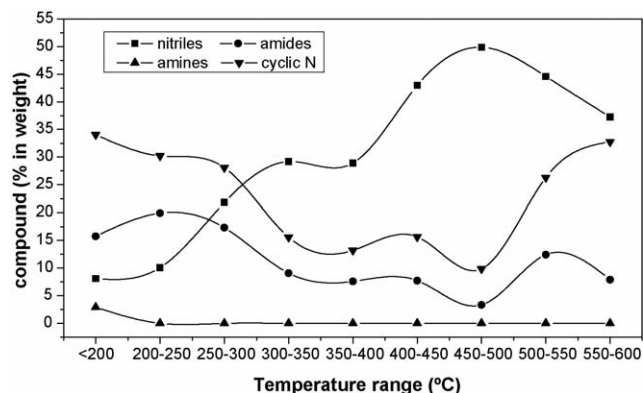


Fig. 12. Evolution of nitrogenated aliphatic compounds (as a percentage of the total tar produced at each temperature) with temperature.

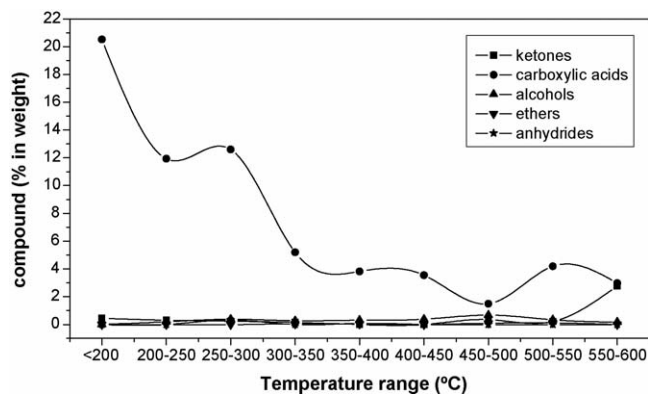


Fig. 13. Evolution of oxygenated aliphatic compounds (as a percentage of the total tar produced at each temperature) with temperature.

200 °C. The main compounds detected are carboxylic acids, which decrease in percentage as the temperature increases (see Fig. 13). Of the other compounds detected, only ketones are present in a significant amount (about 3%) in the tar produced at 500–600 °C.

The results obtained are in accordance with the results obtained by Chaala and Roy [10] in their study of the vacuum pyrolysis of MBM. The compounds observed are similar. Chaala and Roy calculated the higher heating values of the tar (HHV_{tar}) obtaining a value of 34.2 MJ/kg at a final pyrolysis temperature of 500 °C. The tar produced in the current study should therefore have a similar HHV, which turns the tar into a suitable fuel for boilers or gas turbine. Nevertheless, the high amount of nitrogenated compounds could be an environmental problem.

3.3.4. Char composition

Chars obtained at 8 °C/min and different final pyrolysis temperatures were analysed, and the ultimate (dry basis) and proximate analyses of the char at 300, 450, 750, 825 and 900 °C are shown in Table 4. As can be observed most of the decomposition takes place at temperatures lower than 750 °C. From 750 to 900 °C the differences in the percentages of the different elements are small. It is important to analyse the evolution

Table 4
Ultimate (dry basis) and proximate analysis for the char obtained at different temperatures and 8 °C/min

	Char at 300 °C	Char at 450 °C	Char at 750 °C	Char at 825 °C	Char at 900 °C
Element (wt.%)					
C	35.45	35.34	36.24	36.28	36.39
H	1.47	1.46	0.44	0.36	0.34
N	7.31	6.83	5.82	5.20	4.25
O ^a	8.41	7.11	2.27	2.15	4.49
S	0.10	0.08	0.11	0.13	0.10
Component (wt.%)					
Ash	47.26	49.18	55.12	55.88	54.43
Volatile matter	17.55	15.90	6.12	4.60	3.96
Fixed carbon	35.20	34.92	38.76	39.52	41.61

^a Calculated by difference.

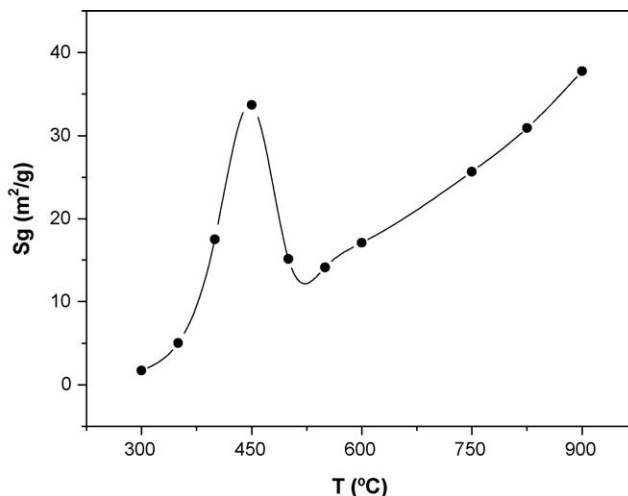


Fig. 14. Evolution of char specific surface area with final pyrolysis temperature for experiments at 8 °C/min.

of the ash percentage with the temperature due to the fact that MBM ash contains metals that can catalyse a gasification process. In Table 4, the ash percentage increases from 300 to 825 °C but decreases from 825 to 900 °C, indicating that some metals could have been evaporated.

3.3.5. Char characterization

The char obtained is hard, compact and easily breakable, due to the melting of the organic substances present in the MBM before their decomposition. As can be seen in Fig. 14, the specific surface area has a local maximum at 450 °C. From 600 to 900 °C the specific surface area increases, reaching its maximum value, 37.7 m²/g, at 900 °C. Char melting was observed to occur at low temperatures, which could cause the decrease of the specific area from 450 to 600 °C. Beyond this temperature, char no longer melts and consequently the area develops as decomposition takes place at higher temperatures.

The morphology of the char prepared at different final pyrolysis temperatures (300, 450, 600, 750, 825 and 900 °C) was also analyzed by scanning electron microscopy (SEM). The images for the six samples are shown in Fig. 15. The observed higher porosity of the char prepared at 900 °C corroborates the higher surface area measured.

The results obtained in this work concerning the effect of the temperature on the MBM pyrolysis process seem to show that it is not worth pyrolysing at temperatures higher than 600 °C from an energy point of view, because beyond this temperature the tar quantity remains constant and the cold gas efficiency hardly increases. However, if the product of major interest from the pyrolysis process were a char with a higher specific area, then higher temperatures would be more convenient.

3.4. Effect of the heating rate on the pyrolysis process

This section describes the study of the influence of the heating rate on the product distribution, product composition and char

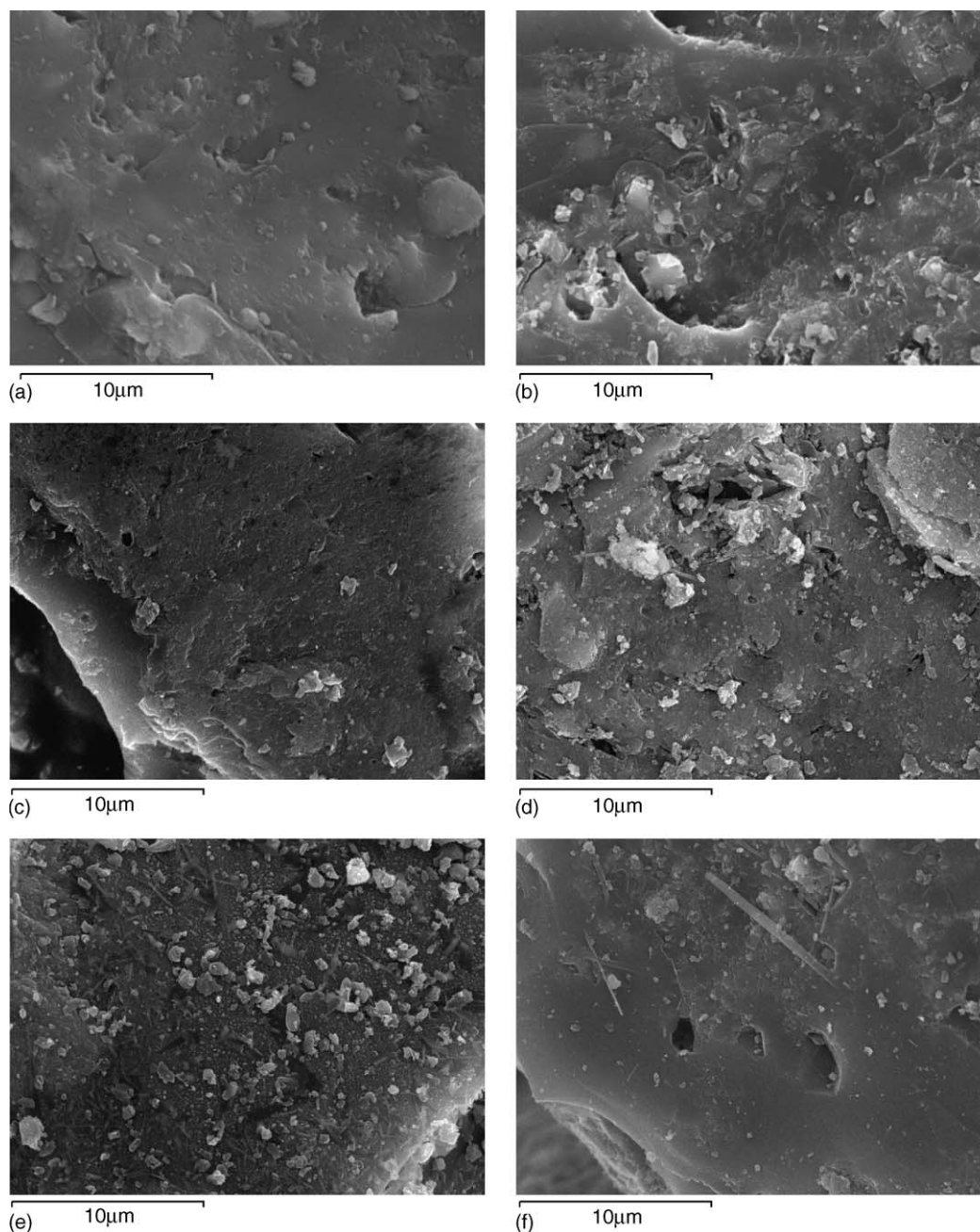


Fig. 15. SEM images of chars obtained at 8 °C/min and different temperatures: (a) 300 °C; (b) 450 °C; (c) 600 °C; (d) 750 °C; (e) 825 °C (f) 900 °C.

characterization for which experiments at three final pyrolysis temperatures (300, 450 and 600 °C) and three heating rates (2, 8 and 14 °C/min) were performed.

3.4.1. Product distribution

Fig. 16 shows the product yields as a function of the heating rate for the three temperatures selected (300, 450 and 600 °C). As can be seen in this figure, the influence of the heating rate on the gas production is practically negligible for any temperature. The percentage of char and tar decreases and rises respectively from 2 to 8 °C/min, but there is no discernible influence of the heating rate from 8 to

14 °C/min. This tendency is the same for all temperatures studied.

3.4.2. Gas composition

The influence of the heating rate on the gas composition was also studied. As can be seen in Fig. 17a, the production of CO rises with the heating rate at any final temperature. No effect of the heating rate on CO₂ production was apparent. It is also observed that the concentration of H₂ has a minimum for the experiment at 8 °C/min at any temperature. Production of CH₄ tends to increase with the heating rate, except for the results obtained at 450 °C and 2 °C/min.

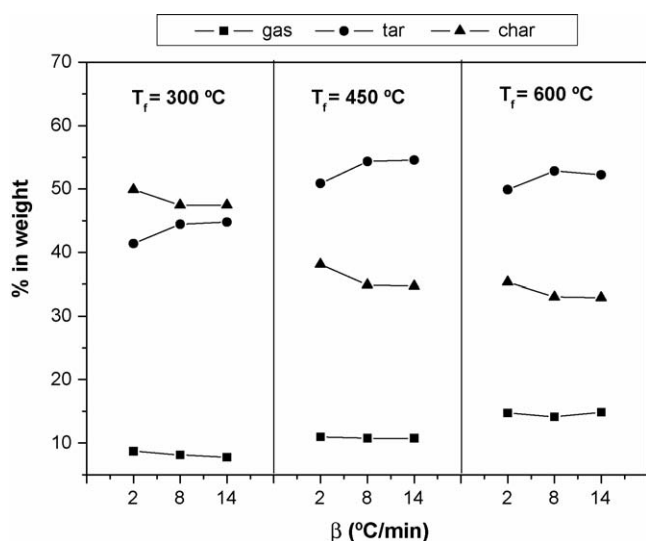


Fig. 16. Evolution of product distribution with heating rate for three different temperatures.

The variation of C_2H_6 , C_2H_4 , C_2H_2 and H_2S concentrations with the heating rate is plotted in Fig. 17b. The influence of the heating rate on C_2H_6 is almost negligible, the percentage of C_2H_4 increases and the amount of C_2H_2 has a maximum at $8^\circ\text{C}/\text{min}$, except for 300°C . The general tendency of the H_2S is to decrease with the heating rate.

In Fig. 18 the evolution of the average low heating value (LHV) with the heating rate is shown. Its value increases with the heating rate except for the experiment at 300°C and $14^\circ\text{C}/\text{min}$, due to the lack of H_2S , C_2H_6 and C_2H_4 . As can be observed in this figure, there is no dependency of the heating rate on the cold gas efficiency from 2 to $8^\circ\text{C}/\text{min}$, whereas it increases from 8 to $14^\circ\text{C}/\text{min}$.

3.4.3. Tar composition

No effect of the heating rate was observed on the tar composition in the range tested. The results obtained at 2 and $14^\circ\text{C}/\text{min}$

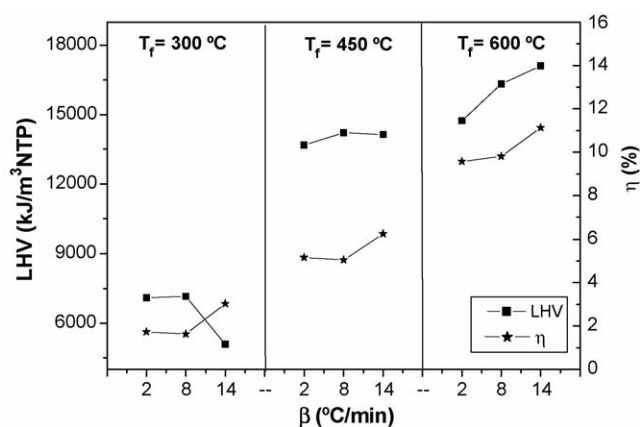


Fig. 18. Lower heating value and cold gas efficiency vs. heating rate for three different temperatures.

are similar to those at $8^\circ\text{C}/\text{min}$. Therefore the tar composition at these heating rates is not shown in this work.

3.4.4. Char composition

Ultimate and proximate analyses of the char obtained at different heating rates and 450°C are shown in Table 5. As can be observed, the percentages of the different elements and components of the char at $8^\circ\text{C}/\text{min}$ are practically the same as the percentages obtained at $14^\circ\text{C}/\text{min}$. However, some differences can be observed between 2 and $8^\circ\text{C}/\text{min}$, for example, the amount of C, H, N, S and volatile matter in the char is higher at $2^\circ\text{C}/\text{min}$ and the percentage of ash and fixed carbon is lower. This indicates that the sample of MBM is less decomposed at $2^\circ\text{C}/\text{min}$ than at 8 or $14^\circ\text{C}/\text{min}$ at the same temperature, which is consistent with the results observed in Fig. 16.

3.4.5. Char characterisation

As can be seen in Fig. 19, the heating rate hardly influences the specific surface area at 300°C . However, the specific surface area decreases when the heating rate increases at 450 and

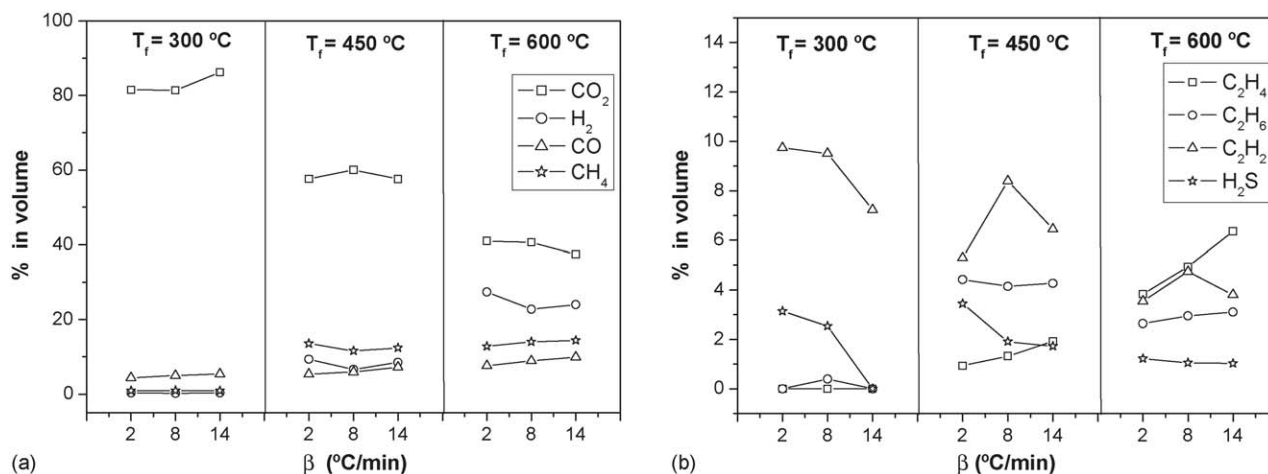


Fig. 17. Evolution of gas composition with heating rate for three different temperatures. (a) CO_2 , CO , H_2 and CH_4 ; (b) C_2H_6 , C_2H_4 , C_2H_2 and H_2S .

Table 5

Ultimate (dry basis) and proximate analysis for the char obtained at different heating rate and 450 °C

	Char at 2 °C/min	Char at 8 °C/min	Char at 14 °C/min
Element (wt.%)			
C	44.80	35.34	34.69
H	3.71	1.46	1.44
N	8.57	6.83	6.54
O ^a	6.85	7.11	6.81
S	0.15	0.08	0.08
Component (wt.%)			
Ash	35.92	49.18	50.44
Volatile matter	35.80	15.90	15.49
Fixed carbon	28.28	34.92	34.07

^a Calculated by difference.

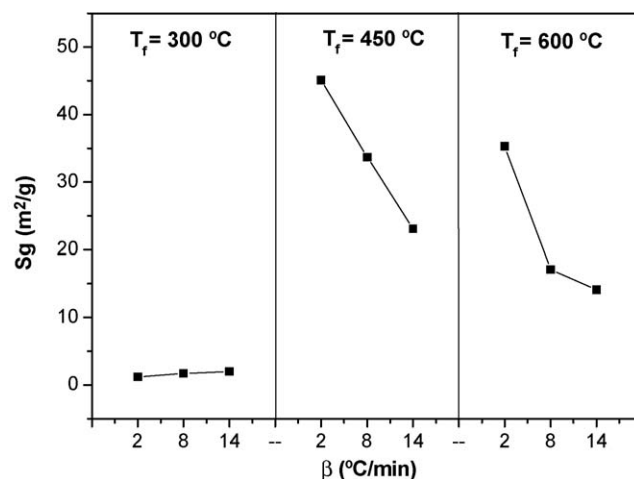


Fig. 19. Char specific surface area vs. heating rate for different temperatures.

600 °C. The effect of the heating rate on the char morphology can also be observed in the SEM images. Fig. 20 shows, as an example, the char microphotography at 450 °C for the three different heating rates tested. The porosity of the char tends to decrease at higher heating rates. The low specific surface area values obtained in this study show that the char resulting from MBM pyrolysis in a fixed bed reactor at low heating rates is not suitable for direct use as active carbon or adsorbent solid.

The results obtained in this work concerning the effect of the heating rate on the MBM pyrolysis process seem to show that, although this effect is not very significant, higher heating rates improve the process from an energy point of view but decrease the quality of the char to be used as adsorbent. Both the LHV of the gas and the cold gas efficiency increase with the heating rates, but the specific surface area of the char decreases.

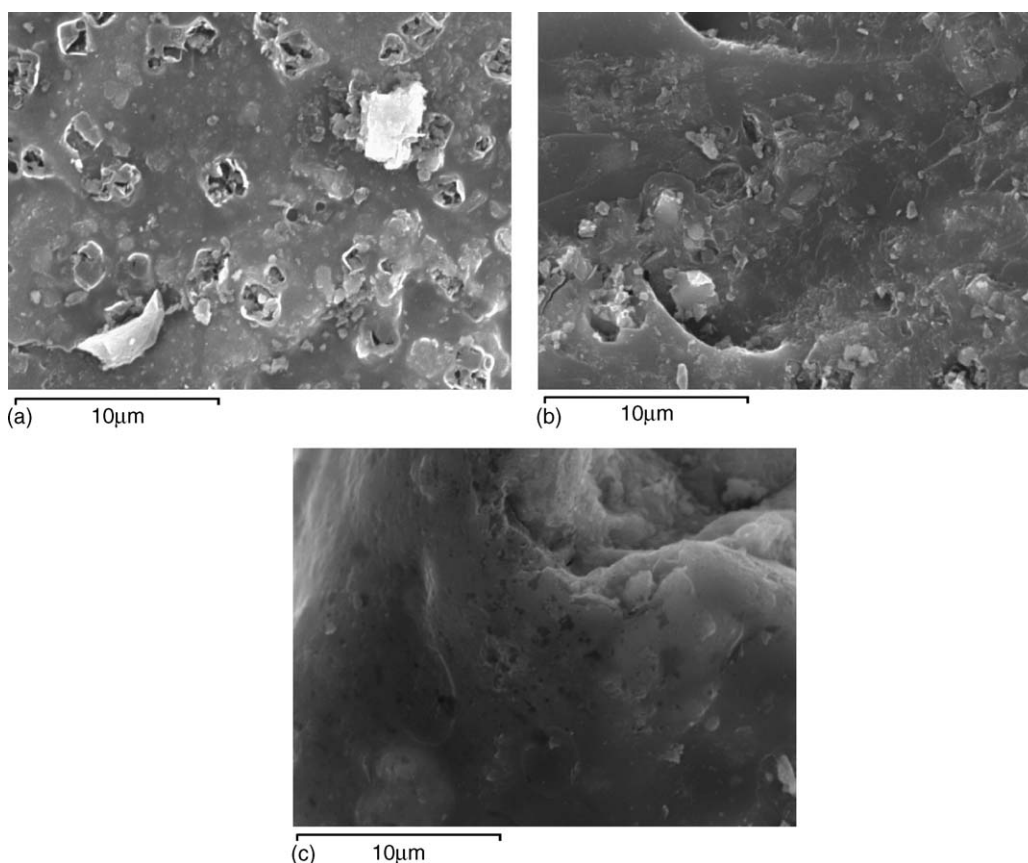


Fig. 20. SEM images of chars obtained at 450 °C and different heating rates: (a) 2 °C/min; (b) 8 °C/min; (c) 14 °C/min.

4. Conclusions

An analysis of the results shows that under the operating conditions studied (300–900 °C and 2–14 °C/min), the final pyrolysis temperature has a greater influence on the MBM pyrolysis process than the heating rate. However, the effect of the heating rate on the temperature profiles inside the sample is significant.

Tar and char are the main products of the process under all the conditions studied. The optimum temperature for obtaining tar is 450 °C (about 55% of tar in weight).

Tar is the product of greatest interest from the point of view of using pyrolysis as a thermal treatment of MBM to obtain energy. On the other hand, since pyrolysis is an endothermic process, the gas fraction can also be important for sustaining the process from an energy point of view. Taking into account that most of the MBM decomposition takes place at temperatures lower than 500 °C at any heating rate, and that the gas production and cold gas efficiency do not increase significantly from 600 to 900 °C, temperatures between 450 and 600 °C are the most appropriate for use of the pyrolysis process to destroy MBM and recover energy. Besides, higher heating rates seem slightly to improve the pyrolysis process for energy valorisation of MBM.

As regards the tar composition, nitrogenated aliphatic compounds are the most significant group at all temperatures and heating rates.

The char obtained has a low specific surface area, the maximum value being 45 m²/g at 2 °C/min and 450 °C. This low value indicates that MBM char obtained under the operating conditions of this work is not suitable for direct use as activated carbon.

Acknowledgement

The authors express their gratitude to the MCyT (Project EET2001-4815) for providing financial support for this work.

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