Bio-syngas production with low concentrations of CO$_2$ and CH$_4$ from microwave-induced pyrolysis of wet and dried sewage sludge

A. Domínguez, Y. Fernández, B. Fidalgo, J.J. Pis, J.A. Menéndez *

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

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Abstract

This paper assesses the feasibility of producing syngas from sewage sludge via two pyrolysis processes: microwave-induced pyrolysis (MWP) and conventional pyrolysis (CP). The changes in the composition of the produced gas as a function of the pyrolysis treatment and the initial moisture content of the sludge were evaluated. It was found that MWP produced a gas with a higher concentration of syngas than CP, reaching values of up to 94 vol%. Moreover, this gas showed a CO$_2$ and CH$_4$ concentration around 50% and 70%, respectively, lower than that obtained in the gas from CP. With respect to the effect of moisture on gas composition, this was more pronounced in CP than in MWP. Thus, the presence of moisture increases the concentration of H$_2$ and CO$_2$ and decreases that of CO, especially when CP was used. In order to elucidate the behaviour of CO$_2$ during the pyrolysis, the CO$_2$ gasification kinetics of the char obtained from the pyrolysis were investigated. It was established that in microwave heating the gasification reaction is much more favoured than in conventional heating. Therefore, the low concentration of CO$_2$ and the high concentration of CO in the microwave pyrolysis gas could be due to the self-gasification of the residue by the CO$_2$ produced during the devolatilization of the sewage sludge in the pyrolysis process.

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Keywords: Sewage sludge; Pyrolysis; Microwave; Syngas

1. Introduction

Currently the growing demand for energy is largely satisfied by fossil fuels. However, the limited reserves of these fuels along with the environmental concern about greenhouse gases have led to the search for new energy sources. Biomass, which offers a sustainable and renewable energy system with a net zero CO$_2$ impact, is a clear example of alternative energy (Chum and Overend, 2001; McKendry, 2002). It can be processed to generate syngas (bio-syngas), which could be used as a clean alternative to fossil fuels in power generation or for the production of derived liquid fuels such as methanol, dimethyl ether and synthetic diesel (Lv et al., 2007).

Specifically, the present paper deals with sewage sludges, a biomass residue generated in wastewater treatment plants. The disposal of these residues is becoming a serious problem in many industrialized countries due to the constant increase in these wastes, the handling of which is not easy and inevitably gives rise to collateral pollution. At the same time, stricter environmental regulations are making the treatment and disposal of sewage sludge more and more expensive. There are several methods on the market today for treating or disposing sludges, such as aerobic or anaerobic digestion, incineration, landfilling or agricultural application. However, most of these methods give rise to subsequent problems, as a result of which secondary treatments are necessary. Consequently, the search for an economically and environmentally acceptable means of disposal has become a matter of increasing importance in recent years (Houillon and Jolliet, 2005).
A possible alternative to the traditional methods of disposal, just mentioned, is the conversion of sewage sludge into fuels by means of pyrolysis (Shen and Zhang, 2005; Karayildirim et al., 2006). Pyrolysis involves heating the sludge in an inert atmosphere. This process leads to the production of a volatile fraction consisting of gases and tar components, and a carbon rich solid residue. The yields of the pyrolysis products depend on the operating conditions (fundamentally temperature, heating rate and residence time of the volatiles in the hot zone), as well as the experimental equipment employed (Horne and Williams, 1996; Inguanzo et al., 2002). In a previous work the authors showed that the pyrolysis of sewage sludge at high temperature favoured the formation of the gas fraction with a high hydrogen content (Domı´nguez et al., 2006).

Most of the pyrolysis process has been mainly carried out by means of conventional heating. However, in the recent years microwave heating has been considered as an alternative for the pyrolysis of biomass (Kriegerbrockett, 1994; Miura et al., 2000; Miura et al., 2004; Dominguez et al., 2007), coal (Monsef-Mirzai et al., 1992; Monsef-Mirzai et al., 1995), oil shales (Chanaa et al., 1994; El harfi et al., 2000), and various organic wastes (Kenneth, 1995; Appleton et al., 2005). Compared to conventional technology, microwave devices can eliminate or severely reduce heat transfer resistances that are common in conventional chemical processes. This is due to the potential of microwaves to heat the material directly, since the transfer of energy occurs through the interaction of the molecules or atoms within the material. Thus, the main advantages of microwave heating with respect to the conventional process would be: a higher heating efficiency and heating rate, and therefore a greater saving of time (Mujundar, 1995; Jones et al., 2002). Furthermore, this form of heating might favour the “in situ” heterogeneous catalytic reaction between the volatiles evolved during the pyrolysis, the carbonaceous residue formed and the mineral content of the raw material (Zhang and Hayward, 2006).

The purpose of this paper was to compare the microwave and conventional pyrolysis of sewage sludge in the production of syngas (H₂+CO) paying special attention to the generation of greenhouse gases such as CO₂ and CH₄. The influence of the raw material and moisture content on the gas composition was also evaluated. An additional objective of this work was to demonstrate that the CO₂ gasification of the char obtained from the pyrolysis is more favoured in microwave than in conventional heating.

### 2. Materials and methods

#### 2.1. Materials

The starting material consisted of two sewage sludges from urban wastewater treatment plants. Sludge V was subjected to aerobic digestion, while sludge L was digested anaerobically. The sludges were dewatered by centrifugation, after which the samples were collected. Table 1 shows the chemical characteristics of the sewage sludges, whereas Tables 2 and 3 show the main inorganic elements and the trace elements of the sewage sludge.

#### Table 1

<table>
<thead>
<tr>
<th>Chemical characteristics of the sewage sludges</th>
<th>Proximate analysis (wt%)</th>
<th>Ultimate analysis a,b (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>A a</td>
<td>VM a</td>
</tr>
<tr>
<td>V</td>
<td>71.0</td>
<td>31.2</td>
</tr>
<tr>
<td>L</td>
<td>81.0</td>
<td>38.1</td>
</tr>
</tbody>
</table>

M: moisture content; A: ash content; VM: volatile matter content; FC: fixed carbon.

a Dry base.
b Ash free basis.
c Calculated by difference.

#### Table 2

<table>
<thead>
<tr>
<th>Main inorganic element composition of the sewage sludges (expressed as wt% of metal oxides on a dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>L</td>
</tr>
</tbody>
</table>

#### Table 3

<table>
<thead>
<tr>
<th>Trace elements of the sewage sludge</th>
<th>Co</th>
<th>Cr</th>
<th>Pb</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>Cd</th>
<th>Hg</th>
</tr>
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<tbody>
<tr>
<td>(ppm)</td>
<td>3.5</td>
<td>121</td>
<td>246</td>
<td>214</td>
<td>13.2</td>
<td>143</td>
<td>662</td>
<td>9900</td>
<td>2906</td>
<td>919</td>
</tr>
<tr>
<td>L</td>
<td>5.0</td>
<td>163</td>
<td>117</td>
<td>239</td>
<td>42.7</td>
<td>192</td>
<td>1020</td>
<td>17400</td>
<td>1355</td>
<td>1446</td>
</tr>
</tbody>
</table>
heavy metal content, respectively. In order to study the influence of the moisture content on the characteristics of the gases produced, the experiments were carried out, using: (i) the as received wet sewage sludge, with a moisture content of 81 and 71 wt% (L81 and V71, respectively) and (ii) a totally dried aliquot of the sludge (L0 and V0).

2.2. Pyrolysis experiments

The sewage sludges used in this study were pyrolysed in an electrical furnace and in a single mode microwave oven at 1000 °C and were kept at this temperature for 20 min. The sample was placed in a quartz reactor (40 cm length × 3 cm i.d.) and N2 was used as inert gas at a flow rate of 60 cm3 min⁻¹. The reactor with the sample was introduced in the electrical oven, which had been previously heated to the required pyrolysis temperature; consequently the temperature of the sample rose rapidly. In the case of microwave heating, the sample was placed in the same quartz reactor, which in turn was placed in the centre of the microwave guide. Details of this experimental set-up have been described previously (Domínguez et al., 2005). Sewage sludge has a very high transparency to microwaves. It was therefore necessary to mix it with an appropriate microwave receptor to achieve the high temperatures required for pyrolysis. The char obtained in previous experiments from the pyrolysis of the samples at 1000 °C, was used as microwave receptor. In order to explore the possible influence of the addition of char on the pyrolysis, the experiments in the electrical furnace were also conducted in the presence of char. The amounts of sewage sludge and absorber used in each pyrolysis experiment are given in Table 4. The experiments were labelled XY, where X is the sludge and Y is the moisture content.

In the microwave oven the required pyrolysis temperature was reached by varying the microwave power. To reach (and maintain) the temperature of 1000 °C the average power used was 530 W for the dry sludges and 911 W for the wet sludges. In the case of the electric furnace the mean time required to reach the pyrolysis temperature was 9 min, compared to only 5 min in microwave heating.

The temperature of the sample in the microwave experiments was monitored by an infrared optical pyrometer. Accurate measurement of the evolution of temperature during the process was very difficult due to inherent difficulties in measuring this parameter in microwave devices. Nevertheless, for the temperature of the bulk sample, the optical pyrometer was calibrated for different temperatures (in separate experiments) by switching off the microwaves and immediately introducing a thermocouple in the centre of the bulk sample. The emissivity parameter was set in the pyrometer in such a way that the temperature measured by both the optical pyrometer and thermocouple was the same. Once the steady state temperature was reached, the temperature shown by the optical pyrometer could be expected to represent the average temperature of the bulk sample quite accurately.

The volatiles evolved from the pyrolysis of the sample passed through five consecutive condensers placed in an ice bath, the last three of which contained dichloromethane. The liquids obtained in the pyrolysis were divided by centrifugation into an aqueous and an organic fraction. Both phases were separated and the organic fraction dissolved in the dichloromethane was obtained by evaporating the solvent at 40 °C. The carbonaceous residue from the microwave and conventional pyrolysis consisted of the char formed from the original sample and the char that was added. Once the pyrolysis was over, the solid carbonaceous residue was recovered from inside the quartz reactor for subsequent characterizations. The non-condensable gases were collected in 12 l Tedlar sample bags with a polypropylene fitting for sampling. The solid and oil fraction yields were calculated on a dry basis from the weight of each fraction, while the gas yield was evaluated by difference. The non-condensable gases were analyzed in a gas chromatograph Perkin–Elmer Sigma 15 fitted with a TCD (thermal conductivity detector), a Teknokroma 10FT Porapak N, 60/80, a Teknokroma 3FT Molecular Sieve 13X and 80/100 columns were used. The oven temperature was set at 50 °C and the carrier gas flow rate (He) was 20 ml min⁻¹. The injector and detector temperatures were 100 and 150 °C, respectively. The TCD was calibrated with a standard gas mixture at periodic intervals.

Table 4

<table>
<thead>
<tr>
<th></th>
<th>MWP</th>
<th></th>
<th>CP</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>L81</td>
<td>L0 V71 V0</td>
<td>L81</td>
<td>L0 V71 V0</td>
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<tr>
<td>Sewage sludge</td>
<td>21.0</td>
<td>4.09 14.03 4.06</td>
<td>21.0</td>
<td>4.02 14.08 4.01</td>
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<td>Sewage sludge (db)</td>
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<td>4.09 4.07 4.06</td>
<td>3.99</td>
<td>4.02 4.08 4.01</td>
</tr>
<tr>
<td>Absorber</td>
<td>5.19</td>
<td>5.02 5.01 5.03</td>
<td>5.01</td>
<td>5.01 5.01 5.01</td>
</tr>
<tr>
<td>Total (db)</td>
<td>9.19</td>
<td>9.10 9.08 9.09</td>
<td>8.10</td>
<td>9.04 9.09 9.02</td>
</tr>
</tbody>
</table>

Product distribution (wt%, db)

<table>
<thead>
<tr>
<th></th>
<th>Residue</th>
<th>Oil</th>
<th>Gas*</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>59.9</td>
<td>3.7</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>57.8</td>
<td>1.8</td>
<td>40.4</td>
</tr>
<tr>
<td></td>
<td>57.0</td>
<td>4.0</td>
<td>39.0</td>
</tr>
<tr>
<td></td>
<td>55.3</td>
<td>2.1</td>
<td>42.6</td>
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<td></td>
<td>69.3</td>
<td>2.4</td>
<td>28.3</td>
</tr>
<tr>
<td></td>
<td>74.1</td>
<td>1.6</td>
<td>24.3</td>
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<tr>
<td></td>
<td>67.7</td>
<td>2.1</td>
<td>30.2</td>
</tr>
<tr>
<td></td>
<td>68.7</td>
<td>2.3</td>
<td>29.0</td>
</tr>
</tbody>
</table>

db: dry basis; MWP: microwave pyrolysis; CP: conventional pyrolysis.

* Calculated by difference.
2.3. Reactivity measurement

The chars (4 g and particle size 1–3 mm) used for the reactivity experiments with CO$_2$ were obtained by pyrolyzing the L and V sewage sludges at 1000 °C in the electric furnace. The temperatures of the experiments were: 500, 650, 800 and 1000 °C for conventional heating and 350, 400, 500 and 800 °C for microwave heating. Before the reactant gas (CO$_2$) was introduced, the system was heated up to the reaction temperature under N$_2$ atmosphere at a flow rate of 40 ml min$^{-1}$. The CO$_2$ flow rate used in all the experiments was 60 ml min$^{-1}$. The only gaseous components detected in the effluent gas were N$_2$, CO and CO$_2$ which were collected in nine 0.5 l Tedlar bags. The first sample of gases was taken 2 min after the CO$_2$ was switched on to flush out the maximum amount of N$_2$. Each bag was filled with the produced gases for 3 min, so the total reaction time was 29 min.

3. Results and discussion

Table 1 summarizes the main chemical characteristics of the sewage sludges used. As can be seen, the sludge treated aerobically (V) has a higher volatile matter content and therefore a higher heating value than the one treated anaerobically (L). This can be attributed to the fact that aerobic treatment produces sludges with highly degraded organic compounds (Conesa et al., 1998) which are easy to volatilize. A high concentration of ash and oxygen and a high value for the H/C atomic ratio were observed. The high heating values (HHV) of the sewage sludge (dry basis) were found to be between 14 and 16 MJ kg$^{-1}$. Other wastes such as plastics, wood, paper, rags and garbage present HHVs in the 17.6–20.0 MJ kg$^{-1}$ range while coal has a HHV between 14.6 and 26.7 MJ kg$^{-1}$ (Perry, 1984). As regards mineral content, Table 2 shows that the main constituents of the sludges studied were Si, Ca and Al, although other metals such as Fe, Ni, Cu, Cr and Zn were also observed in significant amounts, particularly in the L sludge (see Table 3).

3.1. Product yields

The effect of both microwave and conventional pyrolysis (MWP and CP, respectively) on the distribution of the products during the pyrolysis of wet and dried sewage sludge is shown in Table 4. It was found that the gas and oil yields increased and the char yield decreased when the microwave was used instead of conventional heating. In addition, it was proved that the effect of initial moisture content of the sludge on the product yields also depended on the type of heating. Thus, in CP the presence of moisture favoured the formation of gases and caused a reduction in the production of char, especially in the case of the L sludge. However, the opposite result was found in the case of microwave heating i.e. the pyrolysis of dried sludges produced a higher yield of gases and a lower yield of char than those obtained with wet sludges. As regards oil, the presence of water seemed to increase the yield of this product, above all when microwave pyrolysis was used.

A comparison of the sewage sludges showed that the highest char yield was obtained from the pyrolysis of the anaerobically digested sludge (L) while the highest gas and oil yields corresponded to the sludge obtained aerobically (V).

3.2. Gaseous components

Fig. 1 shows the composition (N$_2$ free-vol%) of the gases produced from the microwave and conventional pyrolysis (MWP and CP, respectively) of dry and wet sewage sludges. These results showed the influence of the pyrolysis treatment and moisture content on the production of H$_2$, CO, CO$_2$ and light hydrocarbons. It was observed that the gas obtained from MWP shows a higher concentration of CO and lower concentrations of CO$_2$ and hydrocarbons than that produced by CP. Thus, MWP produced a gas with a concentration of CO$_2$ and CH$_4$ which was around 50% and 70%, respectively, lower than that obtained in CP. On the other hand, from Fig. 1 it can be also deduced that in the pyrolysis of wet sludge the concentration of H$_2$ increased, whereas the concentration of CO decreased in the product gas. The effect that the moisture had on H$_2$ and CO concentration was more pronounced in CP than in MWP. As a result, the highest production of H$_2$ and the lowest production of CO were reached by the CP of wet sewage sludge.
The low CO yield and the enhancement of the CO2 and H2 concentrations in CP could be due to the fact that the water–gas shift reaction (reaction 1) is more favored in CP than in MWP, especially in the case of the pyrolysis of wet sludge.

$$CO + H_2O = H_2 + CO_2 \quad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \quad (1)$$

This behavior may be due to the fact that the stages of drying and devolatilization occur simultaneously during the pyrolysis of wet sludge in CP. On the other hand, in MWP the water is removed very quickly from the reactor and therefore the extent of the reactions between water and the produced volatiles is not as great as in the case of CP.

The low CO2 and hydrocarbon values observed in the gas from MWP might be due to heterogeneous reactions 2 and 3:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H_{298} = 173 \text{ kJ mol}^{-1} \quad (2)$$

$$\text{CH}_4 \leftrightarrow C + 2H_2 \quad \Delta H_{298} = 75.6 \text{ kJ mol}^{-1} \quad (3)$$

These reactions would be favoured in MWP, due to the high temperatures inside the particles of the char (microwave absorber) even at the commencement of devolatilization. Thus in MWP, hot spots, which might be considered as “micro-plasmas” located inside the dielectric solid, were formed. Here the temperature is much higher than the average temperature of the bed as measured by the optical pyrometer (Menéndez et al., 2007).

Table 5 shows the effect of pyrolysis treatment and moisture content on the syngas and hydrocarbon content (H2+CO and HC, respectively), on the H2/CO and CO/CO2 ratio and on the HHV of the gas. As can be seen, the total concentration of CO+H2 (syngas) is higher in MWP than in CP, with values as high as 94 vol%. Regarding the light hydrocarbons, it was observed that their concentration ranged from 12 to 18 vol% in CP and from 2 to 5 vol% in MWP. The CO/CO2 ratio is much higher in MWP than in CP, their values being between 6 and 11.6 and between 1.3 and 2.8, respectively. On the other hand, the H2/CO ratio increased in CP. Thus, in CP the values of this ratio ranged between 1.0 and 3.8, whereas values close to 1 were obtained in the gas from MWP. It must also be noted that in CP an increase in the moisture produces a decrease in both the concentration of light hydrocarbons and in the CO/CO2 ratio, and an increase in the H2/CO ratio. However, in MWP the influence of the moisture on these parameters seems to be negligible. From Table 5 it is also observed that the calorific value of the product gas increased from 12–13 MJ m⁻³ in MWP to 15–17 MJ m⁻³ in CP, due to the high hydrocarbon concentration in the gas from CP.

Depending on the industrial applications in which raw syngas are to be used, the separation of CH4 and CO2 may or may not be necessary. Thus, the residual CH4 can be reformed with steam to produce more CO and H2 while an amine treatment process can be used for CO2 removal (Tijmensen et al., 2002).

A comparison of the results obtained from the pyrolysis of each sewage sludge, showed that the anaerobically treated sludge (L) produces a gas with a lower calorific value, a higher concentration of H2 and syngas and a lower concentration of hydrocarbons and CO2, than the aerobically treated sludge (V). This may be partly due to the high concentration of specific metals in the L sludge, i.e. Ni which catalyzes the decomposition of methane, K and Na which catalyze the gasification reaction with CO2 and Cr, Cu, Fe or Zn which catalyze the water–gas shift reaction.

3.3. Gasification experiments and kinetic study

In order to corroborate that MWH is able to cause the “in situ” gasification of the char with CO2, a set of gasification experiments were carried out at different temperatures using both MWH and CH. Considering that CO and CO2 were the only gases produced from the reaction, reaction 2 can be said to occur exclusively during the experiments. The conversion of CO2 can therefore be calculated from the concentrations of CO and CO2 in the effluent gas by using the following equation (Bai et al., 2006):

$$X_{CO_2} \text{ (mol%)} = 100 \times \frac{CO \text{ (mol%)}}{CO \text{ (mol%)} + 2CO_2 \text{ (mol%)}} \quad (4)$$

where \(X_{CO_2} \text{ (mol%)}\) is the CO2 conversion at a given time and CO (mol%) and CO2 (mol%) are the concentrations of both gases in the effluent gas determined by gas chromatography.

Fig. 2 shows the results for CO2 conversion (\(X_{CO_2}\)) at different temperatures with time using MWH and CH. Only the results obtained using the char from sludge L are shown, although a similar profile was also found for the char from sludge V. A comparison of the conversions obtained when the reaction was performed under CH with those obtained under MWH reveals significant differences. For example, the CO2 conversion at 1000 °C in CH is similar to that at 800 °C in MWH, i.e. the conversion is practically complete. Conversely, in CH the CO2 conversion at 800 °C is around 40% at the initial stage but then it quickly decreases to about 5%. However, in MWH at 500 °C the values of CO2 conversion are even higher than in CH at 800 °C.

### Table 5

<table>
<thead>
<tr>
<th>MWP</th>
<th>CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>L81</td>
<td>L0</td>
</tr>
<tr>
<td>H2+CO (vol%)</td>
<td>94.1</td>
</tr>
<tr>
<td>H2/CO</td>
<td>1.1</td>
</tr>
<tr>
<td>CO/CO2</td>
<td>11.6</td>
</tr>
<tr>
<td>HC (vol%)</td>
<td>2.2</td>
</tr>
<tr>
<td>HHV (MJ m⁻³)</td>
<td>12.8</td>
</tr>
</tbody>
</table>

MWP: microwave pyrolysis; CP: conventional pyrolysis; HC (hydrocarbon content)=∑C1 – C2; HHV = high heating value.
The CO₂ conversion data were used to determine kinetic parameters such as the constant rate or the activation energy. Assuming a first order reaction with respect to the carbon concentration, reactivity \( R \) is defined as (Radovic et al., 1983):

\[
R(s/C_0^1/\Delta X/C_{18}/C_{19}) = k \quad (5)
\]

where \( k \) is the constant rate \( (k = A \exp(-E_a/RT)) \) and \( X \) is the carbon conversion \( (X = (m_{c,0} - m_c)/m_{c,0}, m_{c,0} \text{ and } m_c \text{ are the initial mass of carbon and mass of carbon at time } t, \text{ respectively}) \). The integration Eq. (5) gives rise to the expression:

\[
\ln(1 - X) = -kt \quad (6)
\]

The weight loss of carbon during gasification is caused by reaction (2). Therefore, it is possible to calculate the conversion of carbon \( X \) from \( X_{CO_2} \) (see Eq. (4)) (Menéndez et al., 2007):

\[
X = \frac{X_{CO_2} \cdot M_{0,CO_2} \cdot 12}{m_{c,0}} \quad (7)
\]

where \( M_{0,CO_2} \) are the initial moles of CO₂ which were made to pass through the char bed for 3 min.

The first order reaction rate constant \( k \) can be calculated for each temperature from the plot of ln (1-X) vs. \( t \). The activation energy \( (E_a) \) was determined by using the Arrhenius plot of ln \( k \) against 1/T in which the slope of the linear plot is \( -E_a/R \). The results are shown in Fig. 3. It can be seen that the \( E_a \) of the gasification reaction was higher in CH than in MWH. Moreover, it was also observed that the char from the sludge L was more reactive than the char from sludge V. These results are in agreement to the higher temperatures reached by the char in MWH and with the higher concentration of Na and K in sludge L than in sludge V, which favoured the gasification reaction with CO₂. Furthermore, the differences in the \( E_a \) values of L and V are greater in MWH than in CH. This may be due to the increase in the catalytic effect of the metals present in sludge L when MWH is used instead of CH, corroborating the capacity of MWH to promote heterogeneous catalytic reactions.

4. Conclusions

From the results of this paper it was shown that MWP at high temperature offers an environmentally disposal option for sewage sludge. Compared to CP, MWP produces more gas and less char. Moreover, the gas from MWP contains a higher concentration of syngas and lower concentrations of CO₂ and CH₄ (around 50% and 70%, respectively) than in the gas obtained from CP. The “in situ” gasification of the char by the CO₂ produced and the decomposition of CH₄ may explain the results achieved by MWP. With respect to the effect of moisture on gas composition, this was more pronounced in CP than in MWP. Thus, the presence of moisture increases the concentration of H₂ and CO₂ and reduces that of CO, especially when CP is used. This seems to indicate that in CP the stages of drying and devolatilization occur simultaneously during the pyrolysis of wet sludge, so that water–gas shift reaction is favored. In order to elucidate the behaviour of CO₂ during the pyrolysis, CO₂ gasification kinetic of the pyrolysis char were investigated. The activation energy values of the gasification reaction were higher in conventional heating than in microwave heating which...
confirms that the self-gasification of the residue with the CO₂ produced during the devolatilization is promoted in MWP.

Acknowledgements

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References