Pyrolysis of Sulcis Coal Part 1: characterization and first results of TG-DSC analyses

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Abstract

A study on the pyrolysis behaviour of a high sulphur sub-bituminous Sulcis coal was set up. To investigate the pyrolysis of Sulcis coal a three phase project was established. In the first phase, after coal characterization, pyrolysis experiments were conducted non isothermally in a thermogravimetric analyzer to determine the influence of the heating rate on the thermal degradation of the sample. Then experiments will be conducted in a tubular furnace on greater amounts of sample with different particle size. In the second phase bench scale pyrolysis tests will be performed in a continuous laboratory rotary kiln of 1 m 50 length and 8 cm i.d. and in the third phase experiments will be conducted on a pilot scale rotary kiln able to treat up to 10 kg/h of coal.

This paper presents the first results of the characterization of Sulcis coal and of part of the experiments performed in TG-DSC.

1. Introduction

Pyrolysis is an important phase in most thermal transformation processes \cite{1} like gasification and combustion although in the latter process, it reaches completion in a very short period of time. It can also be considered as a conversion route to produce liquid fuels, chemicals and gases from coal. During pyrolysis, individual functional groups and part of the macromolecular network of coal are decomposed to produce light gas species and smaller fragments \cite{2} that can condense at lower temperature (tars) causing problems of occlusion and dirtying of pipes. The reactivity of coal towards pyrolysis depends on the pore structure, the pyrolysis conditions, the presence and distribution of mineral matter \cite{3}.

Sulcis coal is considered a low quality coal due to its high content of volatiles and sulphur, which is mostly present in organic form \cite{3}. The pyrolysis process could therefore become a sort of cleaning procedure able to remove part of undesired products, such as tars and part of the sulphur \cite{4}, giving the opportunity to produce a higher quality char for successive gasification or combustion processes, and to treat and valorize tars as a source of aromatic chemicals or as a fuel. In effect, organic and inorganic matter undergo significant changes during a thermal treatment \cite{5}.

There is little information about Sulcis coal in literature. Therefore this study could help to find new useful routes for its utilization.

The study will be composed of different phases from batch laboratory studies to the final application in a pilot scale rotary kiln that will be eventually adapted and modified. It is the
result of a cooperation established between two ENEA research units UTTEI and UTTRI. This study will give the opportunity to compare results obtained in different conditions and to give indications about the application of data obtained in laboratory experiments to a greater scale. In table 1 the main phases of the project are outlined.

| Phase 1: Laboratory testing | Coal characterization  
Evaluation of coal pyrolysis in TGA-DSC  
Evaluation of batch coal pyrolysis in a tubular furnace  
Evaluation of evolved gases with FT-IR |
| Phase 2: Bench scale testing | Evaluation of coal pyrolysis in a continuous rotary kiln (kg/h) with coal trap Tar capture  
Evaluation of evolved gases by GC  
Characterization of the residual char |
| Phase 3: Pilot scale testing | Evaluation of coal pyrolysis in a continuous rotary kiln (kg/h) with water scrubber  
Evaluation of evolved gases  
Characterization of the residual char |

*Table 1* The three different phases of the study on sub-bituminous coal pyrolysis

In Figure 1 the bench scale apparatus located in Trisaia is shown and schematized in Figure 2. It comprises the feeding system, the rotary kiln, cold traps for condensable materials (Tars) alcaline traps for acid gases, a sampling port and a volumetric meter. The maximum temperature achievable in the rotary kiln is 1600°C. The reactor is made of alumina and is 1m50 long, 8 cm i.d. and its volume is 7.79 dm³.

In Figure 3 the schema of the pilot plant is given. It comprises the feeding system, the rotary kiln, a wet scrubber, an air condenser, some particulate filters, a torch and some sampling ports. This system can treat up to 10 kg/h of raw material and the rotary kiln can reach up to 1050 °C.

This paper presents the initial results of coal characterization, and of pyrolysis tests conducted in a TGA-DSC analyzer, to identify the behaviour of this coal during the thermal treatment.
2. Experimental

The Sulcis coal came from Sardinia, Italy. It was crushed in an agate mortar and sieved. The pyrolysis experiments were conducted in a Mettler Toledo TG/DSC 1 Star System cooled with a PolyScience 107A00647 cryostat at 22°C, equipped with GC200 Star System Gas Controller and DSC sensor HSS2. To avoid corrosion problems, balance was constantly purged with N\textsubscript{2} 30 mL min\textsuperscript{-1}. Sample was placed in 70 mL alumina crucibles and a N\textsubscript{2} flow of 150 mL min\textsuperscript{-1} was used. Sample amounts of about 9 mg were used and the investigated heating rates were 5, 10, 20, 50, 75 e 100°C/min. The heating program was as follows: the insert temperature was 50°C, then the sample was heated at 10°C/min to 105°C and held at 105°C for 5 minutes. Successively the temperature was raised at the selected rate until 950°C and held at 950°C for 2 minutes before switching to an oxidizing atmosphere (air 150 mL/min) to clean the furnace.

Proximate analyses were performed using the ASTM E1131 method. Elemental analyses were performed in a ThermoQuest EA 1110 CHNS analyzer equipped with a chromatographic Porapak PQS column and auto sampler. The sample was ground to the desired size, dried overnight, placed into a thin capsule and put into the autosampler.

3. Results and Discussion

The results of proximate and ultimate analysis are presented in table 2. The data show that this coal has a high sulphur content and is rich of volatile matter.
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<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>Sulcis Coal (wt% dry)</th>
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<tbody>
<tr>
<td>C</td>
<td>61.31</td>
</tr>
<tr>
<td>H</td>
<td>4.39</td>
</tr>
<tr>
<td>N</td>
<td>1.67</td>
</tr>
<tr>
<td>S</td>
<td>6.33</td>
</tr>
<tr>
<td>O *</td>
<td>14.12</td>
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<table>
<thead>
<tr>
<th>ASTM E1131</th>
<th>(wt%)</th>
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<tbody>
<tr>
<td>Moisture</td>
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<tr>
<td>Volatile matter</td>
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<tr>
<td>Combustible matter</td>
<td>41.27</td>
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<tr>
<td>Ash</td>
<td>11.66</td>
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</table>

*Oxygen is determined by difference

Table 2  Proximate and ultimate analysis of Sulcis Coal.

In figure 4 as an example the plot of a 100°C/min heating rate run in the TGA-DSC analyzer is shown. The weight loss is in dark, the first derivative of the weight loss curve with respect to time (DTG) is in blue and the DSC plot is in red. All data are normalized. The DTG is very useful for examining stepwise transitions and shows the rate at which mass changes occur, and their starting and closing temperatures. It permits the separation of the mass loss steps into peaks.

![Fig. 4 TGA, DTG and DSC normalized curves for Sulcis coal; heating rate 100°C/min](image)

We can observe that pyrolysis occurred in different phases. Initially moisture was lost at 105°C and the plateau was reached. Then DTG evidenced a little peak between 105 and 300°C with a mass loss around 2% and inflection point at 181°C. This could be possibly attributed to loss of water of crystallization and/or interlayer, or to the disruption of H bonds, and reaction of carbonyl groups or peroxy radicals [1].

The primary devolatilization step’s onset Temperature was 401°C, with an inflection point at 452°C. The mass loss associated with this peak was around 35%. During the first devolatilization, coal loses variety of lower molecular weight organic species, especially aliphatic compounds but also some light aromatics, which are believed to arise from moieties.
bound to the more stable network. Some molecules break along the weakest bonds forming free radicals that recombine abstracting H atoms or between themselves to form volatile species or highly condensed species [5]. The inflection point temperature reflects the stability of the macrorystalline structure of coal and is lower in younger coals such as Sulcis coal [6]. Around 600°C a little shoulder was observed in the main DTG peak and corresponds to the secondary devolatilization where further bond breaking and tar production occurs [5]. The last peak was at 752°C, with a mass loss of about 7% and could correspond to final reactions of condensation and aromatization.

Figure 5 reports the mass losses of the pyrolyzed coal as a function of temperature indicating that increasing the heating rate from 5°C/min to 100°C/min, the DTG peak, corresponding to the temperature at which devolatilization was maximum, and all the phenomena move towards higher temperatures as also observed by [5] and [7].

For increasing heating rates lower differences were observed, i.e. the differences between the 5°C/min and 20°C/min curve were greater than the ones between the 75°C/min and the 100°C/min curve. This is evidenced also in figure 6 where the mass loss recorded at different rates was divided into temperature intervals, to better point out the temperatures at which the bench scale rotary kiln could be operated. At lower heating rates there was more time for the pyrolysates to diffuse from the the bulk solid phase to the gas phase, therefore a greater mass loss was recorded at lower temperatures. At high temperatures this effect became less relevant.
Fig. 6  TGA weight loss divided in temperature intervals for the different heating rates

4. Conclusions

Pyrolysis of a high sulphur sub-bituminous Sulcis coal were performed in TGA-DSC. The investigated heating rates were 5, 20, 50, 75 and 100°C/min. Results showed that Sulcis coal exhibits three main devolatilization peaks, the most important of which occurred in the 350-600°C interval. Increasing heating rates led to onset temperatures and DTG peaks moving towards higher temperatures.

For the successive investigations in the tubular furnace the 350-800°C interval will be chosen while for the investigations in the bench scale plant the focus will be on the main devolatilization interval 350-600°C.

The pyrolysis conditions may affect char reactivity: higher temperatures, longer residence times and lower heating rates can lead to reactivity decrease. More severe conditions can lead to a loss of heteroatoms and a decrease in the number of imperfections that originate the active sites [3]. Inorganic elements can influence the distribution of pyrolysates [8]. Therefore future work will evaluate the pyrolysis products and the effect of particle size both in TGA-DSC and in the tubular furnace before the bench scale testing.

5. References