POSTER

CHARS FROM LOW RANK COAL HYDROPYROLYSIS IN SWEPT FIXED BED REACTOR

AM Mastral, MJ Perez-Surio, MS Callén and R Murillo

Instituto de Carboquímica, CSIC, Apdo. 589, 50080-Zaragoza, Spain

INTRODUCTION

In this paper, results on chars from a low rank coal hydropyrolysis, using a swept fixed bed reactor (SFB), are shown and commented.

When coal is heated, the release as radicals of the mobile material, which at the same time is the more volatile, creates spaces of porosity within their network structure. Simultaneously to the release of the more mobile material, the rearrangement of radicals, by combination, generates more stable molecules, mostly forming six-ring cycles. This is the beginning of a new textural structure leading to a new material whose characteristics will depend on the process variables and on the parent coal (1,2). At higher temperatures the size of the aromatic and hydroaromatic clusters increases developing layers and in general a better ordered structure (3). Increasing the rank of the coal, the heteroatom content diminishes and so crosslinking, due mostly to oxygen groups, is replaced by hydrogen bonds. Because of that, high rank coals, when heated, usually show higher plasticity than low rank coals.

When heating is carried out in hydrogen atmosphere, the released radicals can stabilise by capturing hydrogen and giving low molecular compounds, but part of them stabilise by recombining between themselves conducting to high molecular compounds through repolymerization and condensation reactions. These retrogressive reactions are high dependent on the hydrogen pressure. Temperature process and residence time are also extremely influencing variables (4) as well as the reactor design.

When the released products are forced to go through the coal fixed bed, as it happens using swept fixed bed (SFB) reactors, secondary reactions could be promoted because when the released products go throughout the coal bed, this could be playing the role of the filling of a chromatographic columm (4) retaining some of them selectibily and so increasing their residence time.

As char is composed by the coal inherent mineral matter, the unconverted products and the resulting products from repolymerization and condensation reactions, and these last depend on the reactor, the nature of the char will depend on the reactor design.

This work is focused on the nature of the products retained by the coal bed in a SFB reactor as a function of the coal hydropyrolyis variables, which are responsable of the char characteristics.

EXPERIMENTAL

Experiments were conducted on a low-rank coal from N-E of Spain. Its analyses are: C, 80.17% (daf); H, 7.69% (daf); N, 1.03% (daf); S, 5.68% (df); moisture, 22.05%; ash, 26.93% (df); volatile matter, 48.61% (daf).

The fixed bed reactor was inserted in a laboratory scale pilot plant. A downward flow of hydrogen through the coal bed (5g) was used to drive the conversion products into the cooled trap. The final temperature was held for 10 min or 30 min. The hydrogen was forced to pass at 40 kg/cm^2 pressure and the working flow rates were 0.5 l/min. or 2 l/min.

Gases were collected in a special sampling gas bag and C_1-C_3, CO_x(CO+CO_2) and H_2S percentages were determined by GC.

The liquids were recovered directly from the trap (tars) and by chars Soxhlet extraction (extract) with THF. Data obtained are shown in Table 1.

The extract hydrocarbon types were characterised by TLC-FID in a Iatroscan and the extract hydrogen types by 'H nmr in a Brucker CW-80SY.

Chars have been characterised by elemental analysis

Table 1. Yields obtained from SAMCA coal (MS13) hydropyrolysis, (40Kg/cm2, 0.2-0.5mm).

	400°C				500°C	600°C			
	0.5l/min		2l/min		0.5l/min	0.5l/min		2l/min	
	10min	30min	10min	30min	30min	10min	30min	10min	30min
Conv.(%)	55	45	34	47	49	56	59	65	73
Tars (%)	9	11	13	17	13	15	15	26	29
Extrac(%)	9	14	11	17	1	4	0	1	2
Char (%)	62	69	76	67	66	61	59	55	49

and mineral matter content isolated by LTA and their functional groups have been analysed by FTIR spectroscopy.

RESULTS AND DISCUSSION

Experiments were performed to investigate the influence of the process variables on hydropyrolysis products distribution. Results are shown in Table 1.
The percentages of the products retained on the coal bed but solubles in THF, the extracts, are significative at 400°C, showing different nature than the tars collected from the same processes. At increasing temperatures there is a lowering in char and extract percentages. Keeping constant the temperature at 400°C, there is an extract increase with longer residence times of coal and increasing hydrogen flow rates.
At 500°C and 600°C, the extract percentages are worthless, which could be due to: i) the extracts retained at 400°C are released at higher temperatures and/or ii) by increasing temperatures, these retained products undergo changes which imply their insolubilization. If this later possibility would occur, the amount of char organic component would keep constant. On the other hand, the elemental analysis of the chars shows that the carbon percentages are almost constant however the hydrogen and nitrogen contents diminishe. The hydrogen content lowering is normal because the extracts are more and more condensed with the severity of the process (2) while the carbon content seems to point that the extract insolubilization hypothesis is relevant, but it is not the only reason because the mineral matter percentage gradually increases in the chars with increasing temperatures.
The results seem to show that the char undergoes changes implying hydrogen, oxygen and nitrogen loses but their carbonaceous matrix keeps the carbon content.
The spectroscopic and chromatographic technics applied to the extracts show that their nature is mainly polar, ranging the polar components from 91% to 84%, the aromatic ones from 8% to 13% and their saturated components are always lower than 3%. The hydrogen is distributed: aliphatic, 51%-65%; aromatic, 30%-41% and the highest hydrogen content involved in methoxy groups, 13%, is showed by the extract from 400°C hydropyrolysis for 30 min. According to this data, with the severity of the of the process there is a diminishing in the extract polarity. This corroborates that the extract retained in low severity processes undergoes changes causing the release towards gases and tars of the heteroatoms and hydrogen, with their corresponding lowering, but carbonaceous fundamental structure is strongly retained by the coal bed and responsable of the char properties.

REFERENCES

1. AM Mastral, B Rubio, MT Izquierdo, MC Mayoral, Carbon 30(3),375, 1992
2. AM Mastral, MT IZquierdo, MC Mayoral, C Pardos, The J. of Coal Quality 11,1,1992
3. H March, J Griffiths, Intern, Symposium of Carbon, Toyohasy, Japan, 81, 1992
4. AM Mastral, MT Izquierdo, P Burchill, S J Harbottle, A Lowe, D McCaffrey, D Way, Fuel 73,3, 1994