Textural Changes in Coals during Hydrogenation

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Two coals (one subbituminous and one bituminous) have been hydrogenated without solvent under different experimental conditions. Tests without a catalyst were performed at 300, 350, and 400 °C with a hydrogen pressure of 5 or 10 MPa. Two Fe-catalyst precursors (FeSO$_4$ and red mud) were tested at 10 MPa of H$_2$ and increasing the temperature range up to 500 °C in the case of the bituminous coal. The results indicate that mainly at 400 °C and 5 MPa of H$_2$ important repolymerization reactions take place in the subbituminous coal, generating a large macropore volume in the solid residues. In Fe-catalyzed processes, and independently of the catalytic precursor, 425 °C seems to be a critical temperature. At lower temperatures, the hydrogenation reaction is predominant and the residues show increasing open porosity, at higher temperatures and mainly at 500 °C, the repolymerization processes are predominant, obtaining lower conversion and less porous residues. The repolymerization reactions bring about a blockage of porosity in all pore ranges.

Introduction

The thermal decomposition of coal, besides being an important process in itself, is a step closely related to combustion, gasification, and liquefaction. The breakup of the coal macromolecular network and resulting product formation are controlled by the relative rates of bond breaking, cross-linking, and mass transport.[1] In coal liquefaction, the objectives are to cleave large aromatic molecules into smaller units and to stabilize the molecules and free radicals by the addition of hydrogen, thereby forming products of lower molecular weight.

During a conversion process, there are two types of reactions in competition. On the one hand, there is a depolymerization due, in part, to the release of the mobile component and, on the other hand, there are some retrogressive reactions which cause repolymerization by internal stabilization of the radicals.[2] These retrogressive reactions are extremely dependent on the process temperature and on the residence time.

Using the reflectance of vitrinite, it is possible to show the presence of these retrogressive reactions. A high-reflecting vitroplast or vitrinite residue indicates that condensation reactions predominated.[3,4] Other properties used to infer cross-linking are extract yield,[5] fluidity,[6] and the tar molecular weight distribution.[7] One popular method used to study the cross-linking reaction in coal and char is measurement of the solvent swelling ratio as described by Green et al.[8] This method has been employed to determine cross-link density changes during pyrolysis[9] and liquefaction.[10,11]

The aim of the present work is to study the hydrogenation of coals under different experimental conditions. The results on the balance between hydrogenation and repolymerization processes obtained from the product distribution and pyridine swelling ratio measurements will be related with the porous texture changes observed from one systematic characterization of the solid residues carried out by gas adsorption (CO$_2$ and N$_2$) and mercury porosimetry.

Experimental Section

One subbituminous coal from Mequinenza (Spain) and another bituminous coal from Bagworth (England) supplied by British Coal were selected for this work. Both coals were chemically and texturally characterized. Their proximate and ultimate analyses were carried out following the ASTM method.[12] The mineral matter content was determined in a LTA-302, the C, H, and N content in a LECO-CHN-600, and the sulfur content in a LECO-SC-32. The results obtained are given in Table 1.

The apparent surface area of these coals was determined from the adsorption isotherms of N$_2$ at 77 K (S_{N_2}) and of CO$_2$ at 273 K (SCO$_2$), by applying the BET and the Dubinin–Radushkevich equations, respectively. The area occupied by a N$_2$ molecule at 77 K was taken to be 0.162 nm^2, and that occupied by a CO$_2$ molecule at 273 K, to be 0.183 nm^2. From the adsorption isotherms of CO$_2$, and following the method described in a previous paper,[13] both the mean micropore width (W_m) and the characteristic adsorption energy (E_0) were determined. The gross open pore distribution was estimated in the following pore diameter ranges: V_3, the pore volume contained in pores in the diameter range 50–200 nm, and V_2, the pore volume contained in pores in the diameter range 3.7–50 nm, as determined by mercury porosimetry.

The volumetric swelling behavior of coals was measured with pyridine using Liotta's method.[14] The swelling measurements were carried out by placing approximately 200 mg of the coal sample in a 8 mm i.d. tube and centrifuging for 10 min at 200 rpm. The height of the coal (h_1) was measured. An excess of pyridine was added, the tube was vigorously shaken and

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Table 1. Proximate, Ultimate, and Textural Analysis of Coals

	subbituminous	bituminous
moisture (%)	11.3	13.7
volatile matter (%)	36.5	34.1
ash (%)	21.4	7.6
mineral matter (%)	27.7	11.4
C (%)	44.2	62.5
H (%)	5.4	4.2
N (%)	0.4	1.1
S_{total} (%)	8.7	1.1
S_{CO_2} ($m^2 \cdot g^{-1}$)	128	181
S_{N_2} ($m^2 \cdot g^{-1}$)	10.2	10.4
V_2 ($cm^3 \cdot g^{-1}$)	0.054	0.000
V_3 ($cm^3 \cdot g^{-1}$)	0.028	0.011
W_m (nm)	1.13	1.04
E_0 ($kJ \cdot mol^{-1}$)	21.43	22.61
Q_v	2.28	2.00

centrifuged, and the height (h_2) was measured after 1 month. The volumetric swelling ratio was calculated as $Q_v = h_2/h_1$. The values of all these parameters are included in Table 1. More details of the methodology followed in the characterization of these coals have been described elsewhere.[13]

Iron was added as catalyst to the coal in two different ways: by bubbling H_2S through $FeSO_4$ aqueous solutions with coal in suspension and by powder mixing of red mud, RM (32% Fe_2O_3), with coal. Both the catalyst-containing coals and the parent coals were batch hydrogenated in small tube bomb reactors (160 cm^3) by immersion in a preheated fluidized sand bath. The reactors were loaded with 10 g (daf) of coal, under a hydrogen pressure of 5 or 10 MPa. The residence time was 30 min. After this time, the gases were vented and the reactor contents were quantitatively transferred into dry extraction thimbles for extraction with tetrahydrofuran (THF). Percentages of conversion, residues or chars (THF insoluble), asphaltenes (THF soluble, *n*-hexane insoluble), and oils (THF solubles, *n*-hexane soluble) were determined. The chemical characteristics of the catalytic precursors, the different dispersion methods, the hydrogenation procedure, and calculations have been described in detail elsewhere.[14−16]

Textural parameters of all residues were also determined following the methods described above.

All the hydrogenation experiments were carried out in the absence of solvent in order to eliminate its influence upon the results obtained (coal−solvent reactions, coal swelling, etc). Therefore, the chemical nature and porous texture of coals are not modified, and reaction yields and porous transformations are only related with the degree of hydrogenation of the macromolecular structure of coals.

Results and Discussion

The results of the ultimate, proximate, and textural analyses of the selected coals are summarized in Table 1. The high sulfur content of the subbituminous coal is noteworthy; according to different authors,[17] coals with a high sulfur content are not suitable for combustion because of SO_x formation. They are, however, suitable for hydroconversion, showing a large reactivity because the C−S bonds are weaker than the C−C ones.[16] Texturally, the subbituminous coal shows a more open porosity than the bituminous one, and in both cases the surface area obtained from the CO_2 adsorption isotherm is much greater than that obtained by N_2 adsorption, owing to the diffusion problems of the latter into the coal structure under the experimental conditions employed.

The results obtained in the hydrogenation of the parent coals at 350 and 400 °C and two hydrogen pressures, 5 and 10 MPa, are shown in Table 2. Greater conversions

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Table 2. Percentages of Conversion, Oils, and Asphaltenes

experimental conditions		subbituminous	bituminous
350 °C, 5 MPa H_2	conversion (%)	46.9	10.0
	oils (%)	10.8	2.7
	asphaltenes (%)	23.6	3.8
350 °C, 10 MPa H_2	conversion (%)	49.9	14.0
	oils (%)	10.8	13.6
	asphaltenes (%)	24.4	4.7
400 °C, 5 MPa H_2	conversion (%)	62.3	30.2
	oils (%)	14.9	5.4
	asphaltenes (%)	23.8	15.9
400 °C, 10 MPa H_2	conversion (%)	76.0	39.2
	oils (%)	16.0	8.4
	asphaltenes (%)	23.9	22.4

Table 3. Textural Characteristics of Residues

experimental conditions	S_{CO_2} ($m^2 \cdot g^{-1}$)	S_{N_2} ($m^2 \cdot g^{-1}$)	E_0 (kJ/mol)	W_m (nm)	V_2 ($cm^3 \cdot g^{-1}$)	V_3 ($cm^3 \cdot g^{-1}$)
Subbituminous						
350 °C, 5 MPa	150	1.0	21.04	1.16	0.000	0.028
350 °C, 10 MPa	194	3.9	20.00	1.24	0.000	0.027
400 °C, 5 MPa	146	1.4	21.62	1.11	0.000	0.104
400 °C, 10 MPa	193	1.9	20.13	1.23	0.000	0.046
Bituminous						
350 °C, 5 MPa	170	2.7	22.28	1.06	0.000	0.017
350 °C, 10 MPa	197	2.2	20.66	1.18	0.000	0.022
400 °C, 5 MPa	213	2.0	20.25	1.22	0.000	0.030
400 °C, 10 MPa	202	2.6	20.20	1.22	0.000	0.022

are observed at 10 MPa of H_2 than at 5 MPa, with this difference being greater, mainly in the subbituminous coal, as the temperature increases. At 350 °C the subbituminous coal shows conversions of around 50% whereas conversion of the bituminous coal is even lower than 40% at 400 °C.

Low rank coals are known to have a weaker macromolecular structure than bituminous coals[18] due to the greater concentration of heteroatoms and aliphatic chains (cross-links). Consequently, at the same temperature, the degree of thermolysis is greater in low rank coals, producing a large number of free radicals. If the hydrogen pressure is insufficient to saturate these radicals, condensation or repolymerization reactions between these radicals will take place. These retrogressive reactions lead to the formation of high molecular weight compounds which are insoluble in THF.

With respect to the product distribution, it is noteworthy that, whereas for the subbituminous coal the increase in conversion occurring at 400 °C is accompanied by an increase in oil formation, for the bituminous coal the increase in conversion leads to an increase in asphaltene production. This fact is also due to the different macromolecular structure of both coals, because the large number of weak bonds present in the subbituminous coal structure produce smaller fragments by thermolysis, which increases gas and oil formation.

The nature and characteristics of the solid residues should also depend on the global processes developed inside the reactor, i.e., the balance between hydrogenation and repolymerization reactions. Thus, comparing the textural characteristics of the residues with those of their corresponding parent coal, one can observe that, in general, the residues show a greater surface area (S_{CO_2}) than their corresponding parent coal. A micropore opening is also observed, with a greater increase in mean micropore width (W_m) when the reaction is performed at 10 MPa of H_2. For the residues from the subbituminous coal the mesoporosity determined by mercury porosimetry (V_2), corresponding

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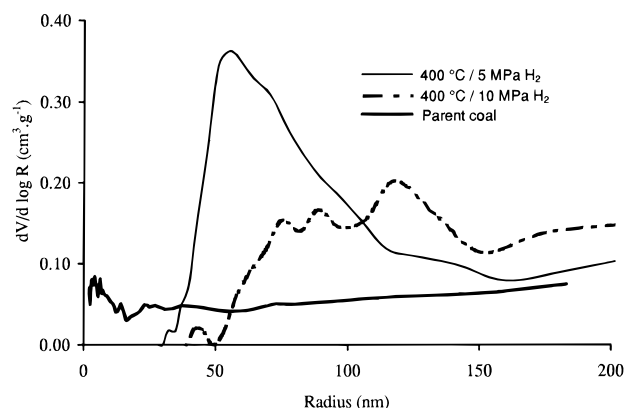
Figure 1. Pore size distribution from mercury porosimetry of the subbituminous coal and its hydrogenation residues obtained at 400 °C.

Table 4. Percentages of Conversion, Oils, and Asphaltenes Obtained for the Subbituminous Coal in the Processes Catalyzed by Fe

experimental conditions	conversion (% daf)	oils (% daf)	asphaltenes (% daf)
FeSO$_4$, 300 °C, 10 MPa H$_2$	25.4	6.8	15.6
FeSO$_4$, 350 °C, 10 MPa H$_2$	75.1	15.7	32.8
FeSO$_4$, 400 °C, 10 MPa H$_2$	89.6	28.4	29.2
RM, 300 °C, 10 MPa H$_2$	21.7	6.1	12.1
RM, 350 °C, 10 MPa H$_2$	60.2	12.8	24.4
RM, 400 °C, 10 MPa H$_2$	95.0	28.5	31.7

to mesopores greater than 3.7 nm in diameter, disappears for all the experimental conditions used; this fact is also corroborated by an increase in the restrictions to N$_2$ diffusion, which produces a decrease in S_{N_2}. Another important textural change observed is that the macropore volume tends to increase with the hydrogenation conversion due to release of the reaction products. However, when the reaction is carried out at 400 °C and 5 MPa of H$_2$, a greater macropore volume is obtained than when using 10 MPa, although the conversion is greater in the latter case.

The pore size distributions obtained from mercury porosimetry for the subbituminous coal and both residues obtained at 400 °C are shown in Figure 1. As mentioned previously, destruction of the mesoporosity and the formation of a large amount of macropores is observed, mainly at 5 MPa of H$_2$.

According to the results shown previously, the hydrogenation processes produce solid residues with a more open porosity than that for their corresponding parent coal, the mesoporosity is transformed in macroporosity, and the mean micropore width increases. The repolymerization reactions, which take place mainly at 400 °C and 5 MPa of H$_2$, produce a large amount of macropores in the hydrogenation residues. Under the experimental conditions studied, these effects are less evident in the residues obtained from the bituminous coal due to the lower degree of thermolysis.

In order to enhance the degree of conversion of these coals, mainly the bituminous coal, two Fe catalysts were tested. For these experiments, and in order to avoid the regressive reactions, the hydrogen pressure was fixed at 10 MPa. The results obtained for the subbituminous coal are shown in Table 4. As expected, conversions increase in comparison to the case for the parent coal (Table 2). This increase is greater at 350 °C when the catalyst precursor is FeSO$_4$ and at 400 °C for RM. With both precursors the percentage of oils increases with increasing temperature; however, the percentage of asphaltenes is
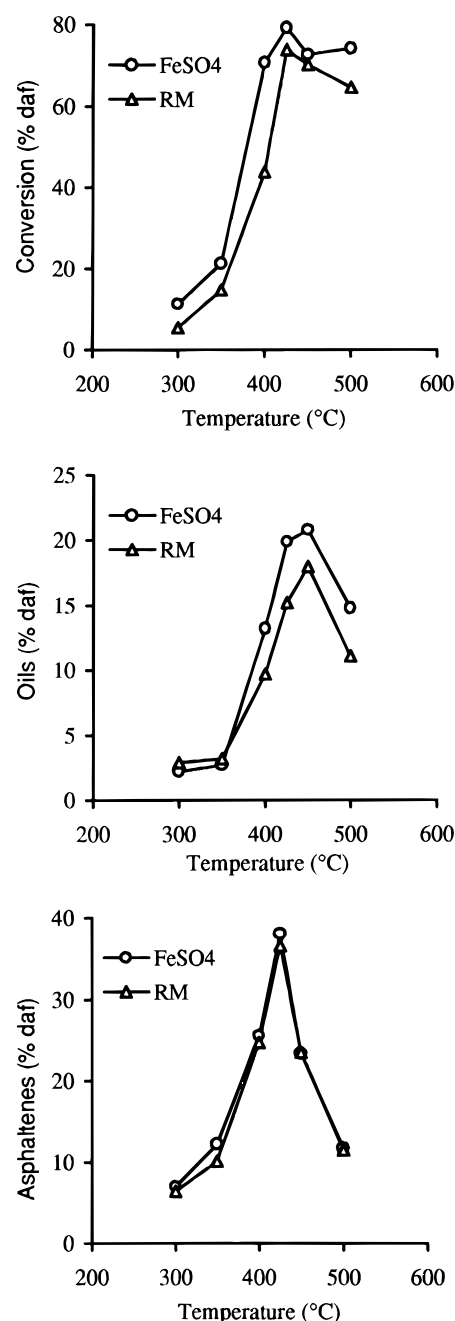

Figure 2. Conversion and product distribution obtained with the bituminous coal in Fe-catalyzed processes as a function of the reaction temperature.

maximum at 350 °C when using FeSO$_4$ whereas for RM it increases with the hydrogenation temperature.

The results obtained for the bituminous coal are depicted in Figure 2. With both catalyst precursors the hydrogenation conversion increases with temperature, reaching its maximum value ($\approx$75%) at 425 °C. The values corresponding to RM are slightly lower mainly due to the lower amount of oils. At 500 °C, the percentages of both product fractions undergo a strong decrease. Between 425 and 450 °C, the hydrocracking process seems to favor oil formation from asphaltenes, while, at higher temperatures, only gas formation and reincorporation of radicals to the solid by regressive reactions are enhanced, consequently increasing the amount of solid residue. The elemental analysis of the solid residues (Table 5) confirms that their carbon content decreases as the temperature increases up to 425 °C, while at higher temperatures it increases again.
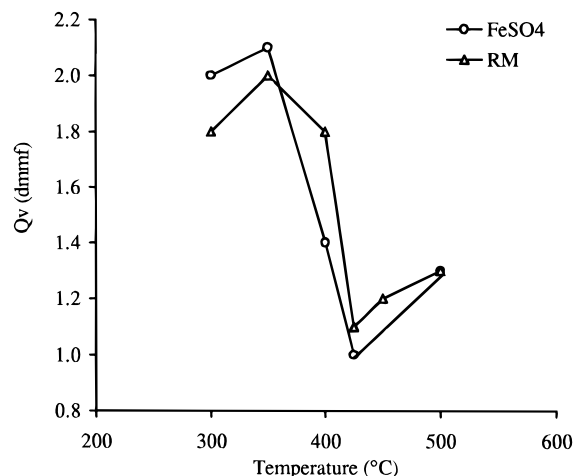
Figure 3. Evolution of the swelling ratio of residues obtained from the bituminous coal in Fe-catalyzed processes as a function of the reaction temperature.

Table 5. Elemental Analysis of Residues Obtained from the Bituminous Coal in Fe-Catalyzed Processes

experimental conditions	C (%)	H (%)	N (%)
FeSO$_4$, 300 °C, 10 MPa H$_2$	68.4	4.8	1.2
FeSO$_4$, 350 °C, 10 MPa H$_2$	67.7	4.8	1.1
FeSO$_4$, 400 °C, 10 MPa H$_2$	54.9	3.0	0.9
FeSO$_4$, 425 °C, 10 MPa H$_2$	48.1	2.4	0.8
FeSO$_4$, 500 °C, 10 MPa H$_2$	65.4	3.0	1.1
RM, 300 °C, 10 MPa H$_2$	58.5	4.3	0.9
RM, 350 °C, 10 MPa H$_2$	57.1	4.1	0.9
RM, 400 °C, 10 MPa H$_2$	40.8	2.3	0.5
RM, 425 °C, 10 MPa H$_2$	36.1	1.9	0.6
RM, 450 °C, 10 MPa H$_2$	42.7	2.2	0.7
RM, 500 °C, 10 MPa H$_2$	48.2	2.2	0.8

As mentioned above, one of the most common methods to follow cross-linking reactions in coal and char is by means of the solvent swelling ratio. Solvent swelling can provide information about the relative changes in cross-linking density, it is assumed that the decrease in swelling is due to the increase in cross-linking. Therefore, the solvent swelling tendency is a qualitative index of the regressive reactions during the hydrogenation process.

In Figure 3 the swelling ratio in pyridine (Q_v) of each residue as a function of the reaction temperature is plotted. It is observed that, independently of the catalytic precursor, this parameter tends to decrease as the temperature increases from 350 to 425 °C, increasing at higher temperatures. These results confirm the enhancement of regressive reactions above 425 °C mentioned previously according to the values of both conversion and product distribution. Up to 425 °C, the hydrogenation reaction causes an increase in conversion and an increase in the residue cross-linking density, while at higher temperatures organic structures of high molecular weight with less cross-linking density are obtained by the reincorporation of the radicals formed to the organic structure of the solid residue.

The differences in the chemical structure of the residues could also be detected by differences in their thermal stability. In order to prove this assumption, the residues obtained at 400 and 500 °C were gasified in air (90 cm^3·min^{-1}), heating at 20 °C·min^{-1} up to constant weight in a Mettler TGA unit, model TA3000. The differential thermogravimetric (DTG) profiles and the evolution of the burn-off (BO) percentage for both residues obtained from the processes catalyzed with RM are shown in Figure 4. Greater BO percentages are observed for the residue obtained at 400 °C at any temperature below 600 °C; however, the maximum gasification rate (DTG peak) is
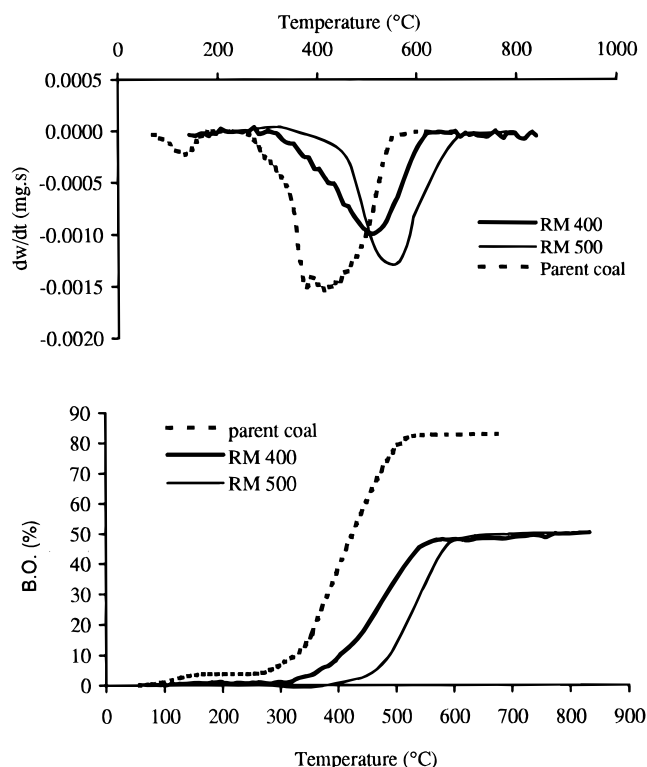

Figure 4. DTG and burn-off profiles for the bituminous coal and some of its hydrogenation residues from RM-catalyzed processes.

Table 6. Textural Characteristics of Residues Obtained from the Subbituminous Coal in Fe-Catalyzed Processes

experimental conditions	S_{CO_2} (m^2·g^{-1})	S_{N_2} (m^2·g^{-1})	E_0 (kJ/mol)	W_m (nm)	V_2 (cm^3·g^{-1})	V_3 (cm^3·g^{-1})
FeSO$_4$, 300 °C	148	3.8	20.19	1.22	0.071	0.038
FeSO$_4$, 350 °C	83	1.7	18.97	1.33	0.087	0.049
FeSO$_4$, 400 °C	64	8.9	18.87	1.34	0.184	0.528
RM, 300 °C	161	4.1	20.52	1.20	0.061	0.066
RM, 350 °C	132	1.9	19.18	1.31	0.073	0.060
RM, 400 °C	74	6.5	18.66	1.35	0.087	0.197

greater in the residue obtained at 500 °C. Nevertheless, it is produced at higher temperature. These results indicate that the formation of high molecular weight compounds by repolymerization reactions leads to a more compact chemical structure and, consequently, increased thermal stability. Similar conclusions can described for the residues from FeSO$_4$-catalyzed processes.

The textural characteristics of the residues obtained from Fe-catalyzed processes for the subbituminous coal are given in Table 6. Only the residues obtained at 300 °C show certain microporosity development with respect to the parent coal, but at higher temperatures the microporosity is progressively destroyed as the conversion increases, generating meso- and macropores. It is noteworthy that while in the noncatalyzed processes the mesoporosity is completely eliminated under similar experimental conditions. In these processes, and independently of the catalytic precursor, this porosity range shows appreciable values, which increase as the conversion obtained increases. The macroporosity also increases as the conversion increases. In conclusion, these residues show a more open porosity as the temperature increases up to 400 °C.

The evolution of the textural characteristics of the residues obtained from the bituminous coal also shows different trends below and above 425 °C (Figure 5). The surface area of the residues from RM-catalyzed processes shows a similar behavior to that described previously for
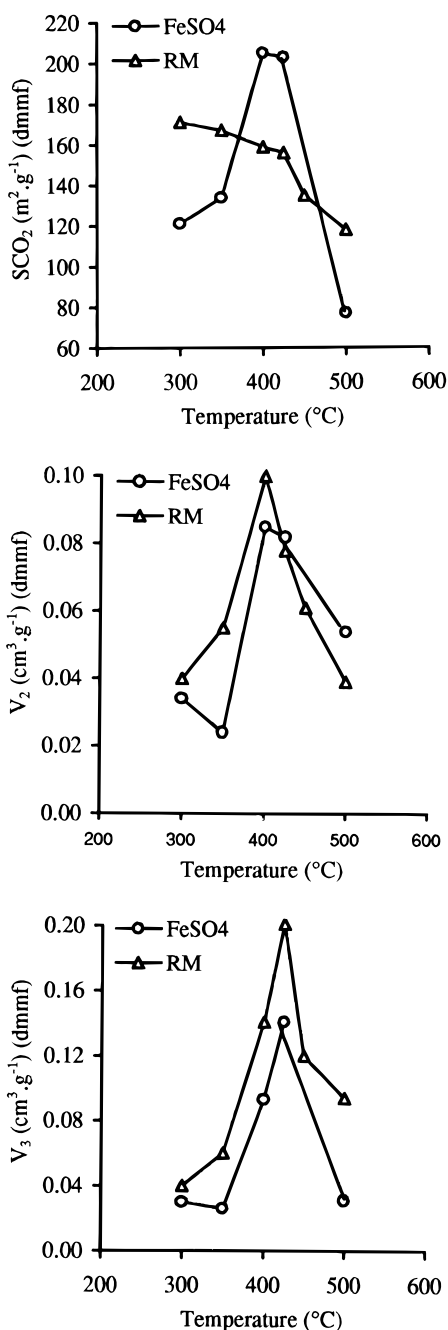
Figure 5. Evolution of the textural parameters of residues obtained from the bituminous coal in Fe-catalyzed processes as a function of the reaction temperature.

residues from the subbituminous coal; thus, this parameter tends to decrease as the temperature increases. However, above 425 °C this decrease is more accentuated. In the case of the residues obtained from FeSO$_4$-catalyzed processes, the surface area increases as the temperature increase up to 400 °C. At 500 °C, however, it undergoes a strong decrease in the residue obtained. The meso and macroporosity increase as the temperature increases up to 425 °C independently of the catalytic precursor. At higher temperatures both parameters decrease; this is probably due to the blockage of porosity produced by the repolymerization reactions.

According to the above results, it is clear that the hydrogenation process provokes an opening of coal porosity. Under mild conditions (300 °C) the conversion is low, obtaining mainly gases and loss of the mobile coal phase, the surface area increases, and the macro- and mesoporosity undergo low increases. Between 350 and 425 °C, the conversion increases and the release of the reaction products produces a large pore opening, mainly as meso- and macropores while the microporosity is destroyed. Due to the fact that the coal surface area exposed to the reagents is located mainly in the microporosity, it must be in this porosity range where the reaction develops to the greatest extent. Thus, the micropores are transformed to meso- and macropores. From 425 °C, repolymerization reactions are favored and reincorporation of radicals causes a blockage of micro-, meso-, and macroporosity.

Conclusions

The subbituminous coal shows a large reactivity even without a catalyst; however, conversions and product distributions are dependent on hydrogen pressure. Lower yields are obtained at 5 MPa than at 10 MPa of H$_2$ at any temperature. As at a given temperature the degree of thermolysis of coal should be independent of the P_{H_2}, the different degree of conversion found for both H$_2$ pressures should be due to the formation of insoluble products by repolymerization reactions. This difference is greater as the temperature increases, which indicates that the repolymerization degree also increases with temperature. The original mesoporosity is destroyed whereas at 10 MPa a more accentuated micropore opening was observed. The repolymerization reactions produce mainly a large macropore volume.

In the noncatalyzed processes, the bituminous coal shows a low degree of conversion, and therefore, the influence of the hydrogen pressure is lower than that for the subbituminous one, although the hydrogenation also provokes a pore opening mainly in the micro- and macroporosity.

The residues obtained in the Fe-catalyzed processes from the subbituminous coal at 300 °C present greater surface area than the original coal. At 350 and 400 °C, however, the microporosity is destroyed, generating meso- and macropores.

The bituminous coal presents increasing conversion up to 425 °C; above this temperature the repolymerization degree increases, producing a decrease in the oil and asphaltene formation while the production of gases and solid residues increases. The evolution of the textural characteristics of these residues, mainly the meso- and macroporosity, is parallel to both the conversion and product distribution.

While hydrogenation processes are predominant, an opening of porosity is observed by the release of reaction products; when the repolymerization processes are predominant, the reincorporation of radicals to the macromolecular structure produces a blockage in all the porosity range.