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Synergetic effects in the co-pyrolysis of coal and petroleum residues: influences of coal mineral matter and petroleum residue mass ratio

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Abstract

The influence of coal and mineral matter nature, and the coal/petroleum residue weight ratio, on the synergetic effects observed when coal and petroleum residues are copyrolysed has been studied. Two coals (Samca, a subbituminous one, Figaredo, a bituminous one, and a demineralised Samca coal) and three-coal/petroleum residue ratio (70/30, 50/50 and 40/60) have been used. Pyrolysis runs were carried out at analytical scale, by pyrolysis-gas chromatography in a pyroprobe 1000 CDS at 900°C and at atmospheric pressure. Synergetic effect on the yield of the main pyrolysis products has been evaluated and discussed with attention focused on valuable feedstock petrochemical products such as light olefines and light aromatic compounds. It is concluded that the intensity of the synergetic effects depends on the coal nature. In the Samca coal with petroleum residue mixtures, the increase in petroleum residue ratio promotes the production of light olefins, disfavouring the production of aromatic compounds. In contrast, for the Figaredo coal, petroleum residue ratio has not a significant influence on the synergetic effects. Coal mineral matter seems to play a negative effect on synergetic effects since an increasing of synergetic effect in light olefins and BTX has been observed after demineralisation of the Samca coal. However, this effect could be attributed to both, the removing of the mineral matter and the changes produced in the porous structure of coal by the acid treatment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Copyrolysis; Coal; Petroleum residues; Synergy

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1. Introduction

Pyrolysis of coal is a good method for producing chemicals like BTX and light olefins, but the yields of these products are limited because of low hydrogen to carbon ratio in coal [1,2]. To increase the liquid yields obtained from coal pyrolysis, the stabilisation of the radicals produced during the breaking reactions should be promoted, and simultaneously, the cross-linking reactions that increase char formation should be decreased [3,4]. For that reason, it is necessary to supply H_2 to coal from other sources. One of the most promising ways is to provide it from hydrocarbon materials, especially hydrocarbon wastes.

Treatment of wastes is one of the most important concerns of modern society. Pyrolysis of wastes of hydrocarbon nature like tires, plastics, oils has been widely studied [5–12]. Pyrolysis appears to be a technique used which is able to reduce a bulky, high polluting industrial waste, while producing energy and/or valuable chemical compounds. One of the main characteristics of these materials is that they have a high hydrogen content and for that reason they could be used as a source of hydrogen in co-pyrolysis reactions with coal [13–16]. Petroleum residues, PR, which are hydrogen-rich compounds, can also act as H_2 donors in these types of processes. In our previous work [17,18] we have shown that there is a synergetic effect for the production of some interesting compounds like light olefins and BTX when coal and petroleum residue are co-pyrolyzed. These effects have been analysed particularly by the evaluation of the influence of different experimental variables like temperature, pressure and coal nature. In this paper, our attention will be focused on two different points:

1. To state the extent of the occurrence of synergetic effects is affected by the petroleum residue mass ratio in the mixture. The different influence of PR mass ratio when two different coals are used will also be evaluated.
2. To state the influence of mineral matter of coal in order to understand which part of the differences observed when PR is co-pyrolyzed with two different coals, can be attributed to the different content and nature of the mineral matter.

2. Experimental

Pyrolysis runs were carried out at analytical scale, by pyrolysis-gas chromatography in a pyroprobe 1000 CDS. The device has been described in our previous work [17]. This kind of experimentation has several advantages. Short periods of time are required for each experiment since the total heating process lasts 20 s. In addition, the probe can be easily linked on-line to the gas chromatography which prevents the loss of the less heavier compounds in the tubes.

The nominal temperature used was 900°C and pressure was 0.1MPa.

One selected run was repeated five times to calculate the experimental error. The CI calculated this way was in all cases below 1%. The other runs were repeated twice and the mean value was assumed as the true value.

2.1. Coal/petroleum residue samples

Two coals, Samca and Figaredo and a petroleum vacuum residue (PR) were used in this work. Samca is a subbituminous coal, with high volatile content, and Figaredo is a bituminous one, of higher rank, with low volatile content. The petroleum residue is produced from the distillation of different crudes and has been submitted by REPSOL, Puertollano. The main characteristics of these materials are shown in Table 1. Different experimental series were carried out using mixtures with a mass ratio (coal/PR) of 50/50 and 40/60, which will be compared with the results obtained for 70/30 mixtures [17].

Preparation of the samples was as follows: the petroleum residue was first solved in THF and then the coal was added. The mixtures were subsequently sonicated. After 15 min, heating under vacuum evaporated THF. The dried samples are grounded to <0.2 mm. A cryogenic grounding technique was used in order to increase the grindibility of the sample and to improve the homogeneity of the mixtures.

To evaluate the role of mineral matter of Samca coal, a sample was demineralised and afterwards, it was co-pyrolyzed with petroleum residue. The demineralisation procedure was as follows: 20 g of coal was mixed with 70 ml of ClH and water. The mixture was heated (60°C) for 30 min. It was then filtered and the coal was washed with a volume of distilled water five times higher than that used for the demineralisation. Finally the coal was heated in a vacuum stove until complete water evaporation occurred.

2.2. Analytical methods

Gases were analysed by GC using two separate analytical methods: an alumina column with helium as carrier and FID detection for C_1–C_6 hydrocarbons; two packed columns: Molecular sieve 13 × and Porapak with helium as carrier and TCD detector for permanent gases. Hydrocarbons chromatographied between *n*-pentane and *n*-hexane were accounted for together as C_5. In the same way, compounds chromatographied between *n*-hexane and benzene were accounted for as C_6. Quantification of gas components was carried out by means of standard gas mixtures.

Compounds eluted from benzene to chrysene ($>C_6$ compounds) were analysed by GC/MS. Using a computerised library of mass spectra identified most of the

Table 1
Proximate and ultimate analysis of the samples (dry basis and daf basis)

	Ash	Volatiles	C	H	N	O	S
Samca	22.8	36.9	75.9	5.3	0.7	12.3	5.8
Figaredo	3.9	17.1	91.2	4.2	1.8	0.6	2.3
PR	0.2	80	83.41	9.75	0.55	0.98	5.3

Table 2
Yields (%wt) of main compounds obtained in the copyrolysis of 50/50 and 40/60 mixtures

T (°C)	Samca/RP			Figaredo/RP		
	70/30	50/50	40/60	70/30	50/50	40/60
CO	5.4	7.0	5.5	1.4	1.0	1.0
CO_2	7.7	5.1	4.9	1.6	1.9	1.6
SH_2	2.1	1.8	1.9	0.6	0.6	0.9
CH_4	3.8	7.6	6.3	7.7	7.0	7.6
C_2H_6	0.4	0.7	0.5	0.6	0.8	0.9
C_3H_8	0.1	0.1	0.1	0.1	0.2	0.2
C_4	0.5	0.9	0.8	0.6	0.8	0.9
C_5	0.2	0.3	0.2	0.3	0.3	0.2
C_6	0.3	0.6	0.3	0.3	0.4	0.5
Benzene	0.7	03	0.4	0.4	0.4	0.5
Toluene	0.4	0.3	0.3	0.3	0.3	0.3
Xylene	0.2	0.1	0.1	0.1	0.1	0.1
Alkyl-benzene	0.4	0.6	0.9	0.4	0.4	0.5
Naphthalene	0.3	0.2	0.2	0.2	0.2	0.2
2,3 rings	0.3	0.3	0.6	0.3	0.9	1.0

compounds present in liquids. Tri and tetra methylbenzene was accounted for as alkyl-benzenes. All compounds chromatographied between naphthalene and phenanthrene were accounted for as 2,3 rings. Quantitative composition of liquids was determined by a solution of external standards.

For the study of the C_1–C_6 fraction, the pyroprobe was not directly linked to the chromatograph. The experimental device has been described in previous work [17].

A different experimental device was used for the $> C_6$ compounds. In this case, the pyroprobe was linked to the chromatograph in order to avoid condensation of the heavier compounds on the tubes. The set up has been also described in our previous work [17].

3. Results and discussion

3.1. Evolution of yields

The yields obtained from the pyrolysis of both coals and PR alone and those of 70/30 mixture were shown in our previous work [17,18] and are summarised in Table 2. Table 2 also shows the yields for the main gaseous compounds for Samca and Figaredo/PR mixtures 50/50 and 40/60. It can be noted that the main yields (CO, CO_2 and H_2S excepted) are obtained for methane and light olefins, especially ethylene and propylene. The higher yields are obtained for the mixture 50/50 of Samca coal. These products are mainly obtained by the cleavage of paraffinic chains from petroleum residue.

The evolution of $>C_6$ is also shown in Table 2. It should be noted that there are only slight differences for BTX yields when 50/50 and 40/60 mixtures are compared. The higher differences appear for 2,3 ring compounds whose yield increases as does the PR ratio.

Table 3 shows the yields obtained for the C_1–C_6 compounds when Samca coal is demineralised and mixed with the residue. After demineralisation of Samca coal, gaseous compounds, especially methane and light olefins increase, compared to the yields obtained for the untreated coal [17]. The same trend is observed for all mixtures especially for 70/30 and 50/50 ones.

The yields obtained for $>C_6$ compounds Table 3 are similar to those obtained for coal and 70/30 mixture before demineralisation.

3.2. Evolution of synergism

The evaluation of the interactions between coal and PR has been carried out in all cases by comparing the yields of the co-pyrolysis of the mixture (experimental yields) and those obtained by the linear compbination of the pyrolysis yields of coal and petroleum residue (calculated yields). The percentage of increasing or decreasing of the experimental yield with respect to the calculated yield is called synergetic effect.

Table 3
Yields (%wt) of the main compounds obtained in the pyrolysis of demineralizated Samca coal and the mixtures with PR

	Demineralizated	70/30	50/50	40/60
CO	10.0	8.4	4.7	5.2
CO_2	10.2	6.7	5.5	5.6
SH_2	2.8	2.4	2.0	2.2
CH_4	3.2	6.6	5.5	6.0
C_2H_6	0.1	0.6	0.8	0.4
C_2H_4	0.5	3.7	6.1	3.9
C_3H_8	0.03	1.0	0.2	0.1
C_3H_6	0.2	1.4	2.1	1.0
C_4	0.1	0.8	1.1	0.6
C_5	0.1	0.3	0.4	0.5
C_6	0.1	0.5	0.4	0.3
Benzene	0.3	0.7		
Toluene	0.2	0.4		
Xylene	0.1	0.1		
Alkyl-benzene	0.2	0.7		
Naphthalene	0.05	0.2		
2,3 ring	0.03	0.2		

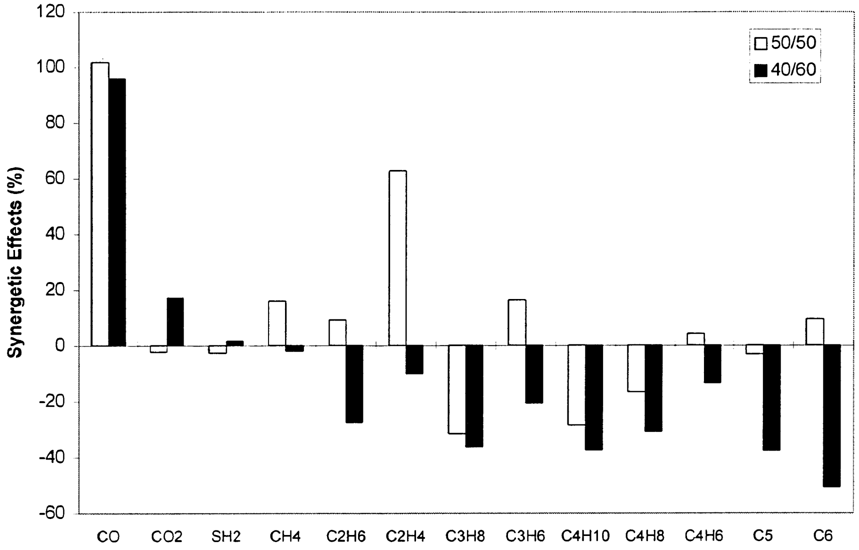

Fig. 1. Synergetic effects for the C_1-C_6 compounds obtained in the co-pyrolysis of Samca/PR mixtures: 50/50 and 40/60.

3.3. *Influence of the PR ratio in the mixture*

3.3.1. *Mixtures with Samca coal*

Fig. 1 shows the synergetic effects obtained for the yields of the C_1–C_6 compounds obtained in the co-pyrolysis of mixtures 50/50 and 40/60 of Samca coal and PR. The results obtained with the 70/30 mixture has been already shown in our previous work [17].

For the 50/50 mixture there is an experimental increase in the yield of CO, CH_4, C_2H_6, C_2H_4, C_3H_6 and butadiene comparing with the calculated values. The synergetic effect is especially high for methane (16.6%) and light olefins like ethylene (62.7%) and propylene (16.3%). The other compounds show no synergetic behaviour and the experimental and calculated values are similar. In some cases, like CO_2 and C_4 compounds, the experimental yields are lower than the calculated ones, so that the synergetic effects are negative.

An increase in the amount of PR in the mixture enhances the production of methane and ethylene and disfavours the formation of CO_2. As has been previously stated [19,20] the CO_2 formation is related with cross-linking processes, very typical of coals with a high oxygen content like Samca coal and therefore the presence of petroleum residue in the mixture seems to reduce considerably these cross-linking reactions.

Mixture 40/60 shows a rather different behaviour, there is an experimental increase compared with the calculated yields for CO (95.7%) and CO_2 (17.1%) production and a slight decrease for all the other C_1–C_6 compounds, even ethylene and propylene. For this mixture, there is a similar trend to that shown by the 70/30 one [17] but no synergetic effect is observed for the production of ethylene. The higher PR mass ratio in the mixture disfavoured the synergism such as happened working at 1MPa [17]. In summary it can be observed for the C_1–C_6 compounds that the improvement of the synergy obtained when PR mass ratio increases from 30 to 50% disappears when this ratio increases even more.

Fig. 2 shows the synergetic effects for $> C_6$ compounds for both mixtures. For mixture 50/50, it should be noted that the experimental yields of aromatic compounds as a whole decreases, compared with the calculated one. BTX, naphthalene and 2,3 ring compounds show a negative value for the synergetic effect. In contrast, there is a positive synergetic effect for alkyl-benzenes. The 40/60 mixture shows a similar behaviour and there is an even higher synergetic effect for alkyl-benzenes production. This fact seems to confirm that these groups of compounds are obtained from the degradation of complex structures of petroleum residue rather than from amortisation reactions.

Different types of reactions have been reported for the pyrolysis of coal and petroleum residues [21,22]. Most of them are degradation processes as well as recombination and Diels–Alder reactions. If the predominant pathways of the co-pyrolysis were recombination and Diels–Alder reactions, there would be an increase in the production of BTX and a decrease of light olefins. However, the accurate description of the mechanism of this type of process is not an easy task, as pyrolysis of these types of materials involves a multitude of single reactions proceeding simultaneously that cannot be easily controlled [23–25]. For 70/30 mixtures [17] the experimental yields of all aromatic compounds were higher than the calculated ones and so that, recombination reactions were supposed to lead the

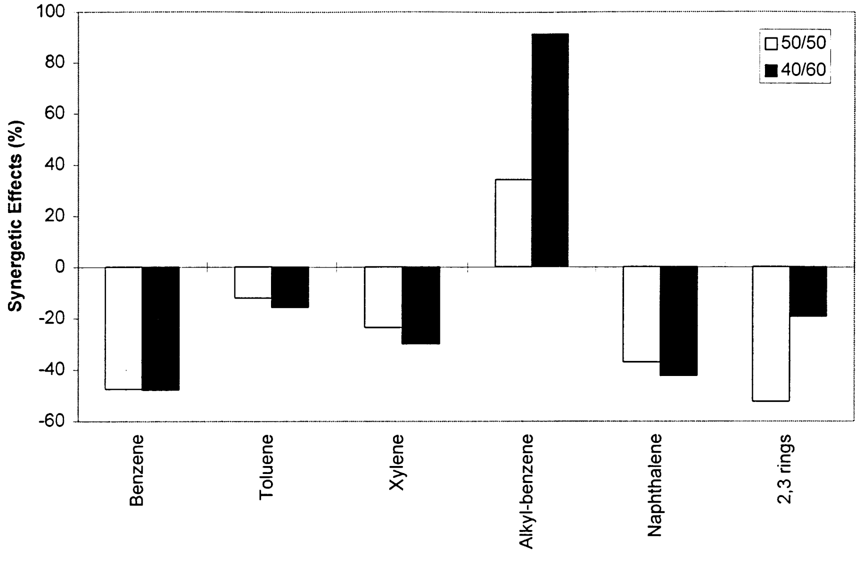

Fig. 2. Synergetic effects for the $> C_6$ compounds obtained in the co-pyrolysis of Samca/PR mixtures: 50/50 and 40/60.

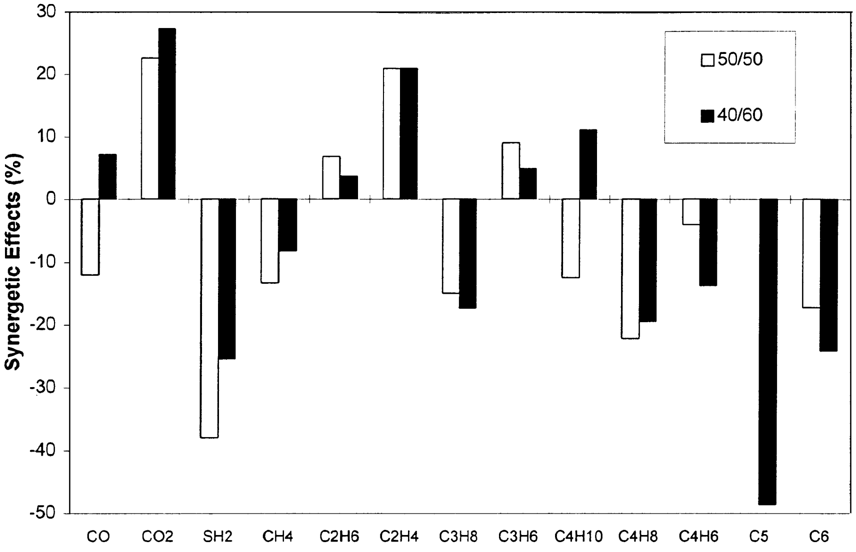

Fig. 3. Synergetic effects for the C_1–C_6 compounds obtained in the co-pyrolysis of Figaredo/PR mixtures: 50/50 and 40/60.

process. On the contrary, for the 50/50 mixture, the calculated yields of the aromatic compounds were always higher than the experimental ones, and so that the value for the synergetic effect is negative. This is important evidence because of the fact that the natures of the interactions between coal and petroleum residues are affected by the PR amount in the mixture. An increase in PR ratio promotes the reactions that leads to the production of gaseous compounds, especially light olefins, that probably proceed from the degradation of the residue. On the other hand these olefins can not easily undergo secondary reactions so that aromatic compounds production is not enhanced. This effect disappears when the PR ratio increases to 60%, in this case neither light olefins nor BTX production is enhanced after co-pyrolysis.

3.4. Mixtures with Figaredo coal

Fig. 3 shows the synergetic effect for C_1–C_6 compounds after the co-pyrolysis of 50/50 and 40/60 mixtures of Figaredo coal and petroleum residue, at 900°C and 0.1MPa. For the 50/50 mixture, there is a synergetic effect in the production of CO_2 (22.6%), ethane (6.7%), propylene (9.02%) and especially ethylene (20.9%). On the other hand, there is a negative effect for methane (− 13.4%). According to previous works [26,27], methane production is related mainly to coal so that a decrease on coal mass ratio in the mixture would lead to a decrease in methane yields. The important experimental increase observed for CO production for the Samca coal does not appear with Figaredo coal. It should be pointed out that this coal has lower oxygen content than Samca as it does not contain so many phenolic groups.

For the rest of C_1–C_6 compounds, the calculated and experimental yields are quite similar, leading to a value for the effect near to zero. Compared with the 70/30 mixture [17], the behaviour of this one is similar and the observed synergism for ethylene and light olefins is maintained.

For the 40/60 mixture, there is a slight increase for carbon oxide yields. The higher synergetic effects occurs for the ethylene yield (20.9%) apart that for CO_2. The decrease of methane experimental production is also important.

Fig. 4 shows the synergetic effects for the $> C_6$ compounds. For the 50/50 mixture this value is negative except for the highest weight compounds. The same behaviour is observed for the 40/60 mixture.

In summary, it can be concluded that increasing the PR ratio does not influence to a great extent the interactions between PR and Figaredo coal. These interactions are really not very important, as was previously stated for the 70/30 mixture [17], the only effect being that observed for methane production that decreases as Figaredo coal ratio in the mixture decreases. The synergetic trends are similar for mixture 70/30, 50/50 and 40/60. In these cases the important differences observed between 70/30 and 50/50 mixtures with Samca coal are not observed. Neither the degradation of petroleum residue nor the secondary reactions to produce aromatic compounds seem to be promoted by co-pyrolysis.

3.5. Influence of mineral matter

It is well known that mineral matter may not act as an inert compound during coal conversion processes. For example, iron minerals are good catalysts for

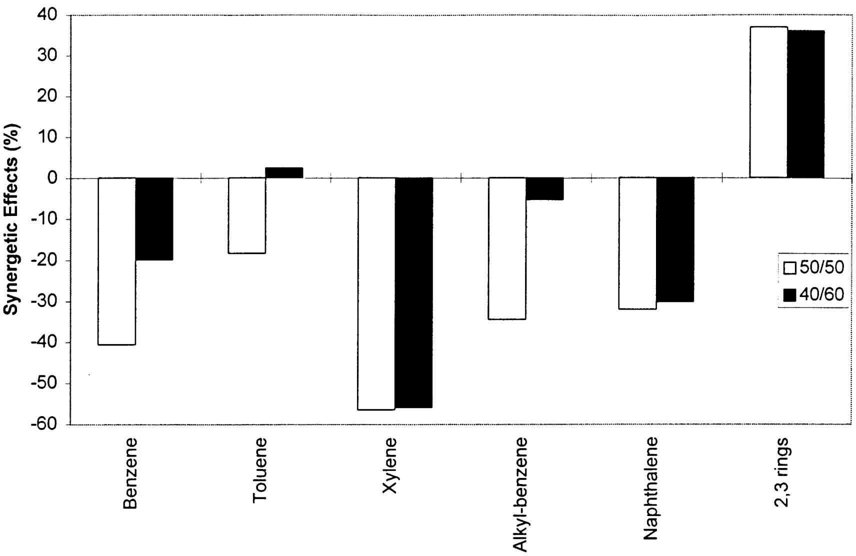

Fig. 4. Synergetic effects for the $> C_6$ compounds obtained in the co-pyrolysis of Figaredo/PR mixtures: 50/50 and 40/60.

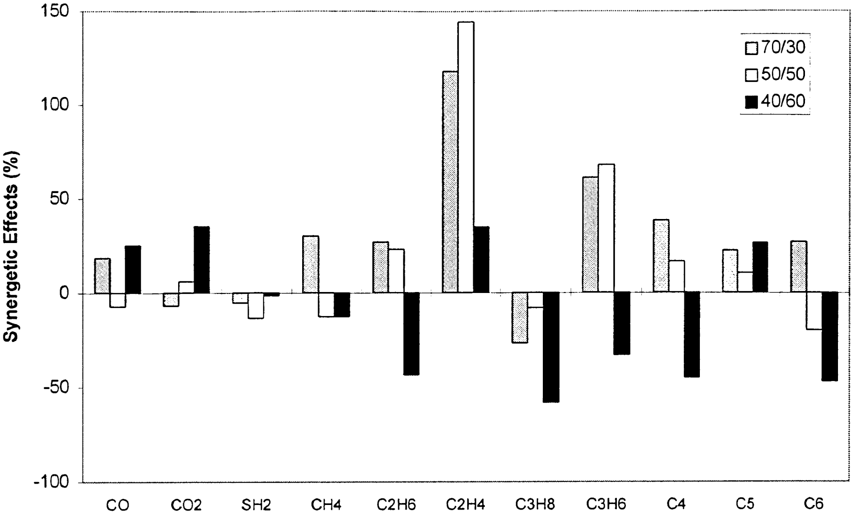

Fig. 5. Synergetic effects for the C_1–C_6 compounds obtained in the co-pyrolysis of demineralized Samca coal/PR mixtures: 70/30, 50/50 and 40/60.

hydrogen transfer during coal liquefaction. Mineral matter from Samca coal contains significant amounts of pyrite and $FeSO_4$ that have been identified as hydrogenation catalysts. The main evidence that an important effect on the mineral matter may occur is the different behaviour observed when coals with different mineral matter composition are co-pyrolyzed with a residue like petroleum residue or lube oil waste [17,28].

As we have previously mentioned for 70/30 mixtures of Samca coal [17], there are interactions in gas phase between radicals that finally lead to higher yields of aromatic products. In order to elucidate the role played by the mineral matter, a study of co-pyrolysis processes using a demineralised coal was carried out.

Fig. 5 shows the synergetic effect obtained in the co-pyrolysis of Samca demineralised coal and PR in a mass ratio of 70/30, 50/50 and 40/60 for the C1–C6 compounds. For the mixture 70/30, there is a positive synergetic effect in the gas phase as a whole, particularly for the production of CO, methane, ethylene, ethane, propylene and butadiene, and a negative value in CO_2 production. The high synergetic effect for ethylene should be noted. For the 50/50 mixture, there is a favourable synergetic effect for ethylene, propylene and butadiene and a negative value for CO and methane. For the 40/60 mixture, the effects are close to zero because the calculated and experimental yields are quite similar for almost any compound except for ethylene and carbon monoxide, which show higher, experimental than calculated values.

For the $> C_6$ compounds (Fig. 6), it can be observed than when a demineralised coal is used, there is also an important synergy for the production for benzene and its mono and poli-substituted derivatives. In summary the 70/30 demineralised coal mixture shows a similar behaviour to the coal mixture because aromatic compounds production is enhanced but, beside this, mineral matter removal also promotes significant synergetic effects in the production of light olefins.

It can be suggested that by removing mineral matter, the yields of volatile compounds are increased, enhancing in this way the transformation processes that happen during pyrolysis. This probably proceeds by disfavouring cross-linking reactions, consequently reducing char formation. Otake et al. [29] studied the pyrolysis of different lignites with a high mineral matter content using a very similar demineralisation procedure to the one used in this paper. They observed that the acid treatment reduced the carboxylic groups that have metals associated, into the hydrogenated forms. This way, after pyrolysis, lower yields of hydrogen, carbon oxides and methane are obtained and, as a whole, liquid yields increase in detriment to char formation. Raavendran and Gray [30,31] who worked on related subjects, showed similar results: lower char formation and important improvements in tar formation when mineral matter is eliminated. These authors also pointed out that by eliminating mineral matter the release rate of volatiles from solid matrix pores increases, and occlusion phenomena are reduced and the adsorbent properties of the resulting materials are improved.

In spite of the fact that the results showed in this paper agree with those previously mentioned, it can not be firmly concluded that the high synergetic effects observed after demineralisation were only due to the elimination of mineral matter. The observed increase in both volatile compounds release and gas phase interactions might be a consequence of the acid treatment and not only of the presence or absence of mineral matter.

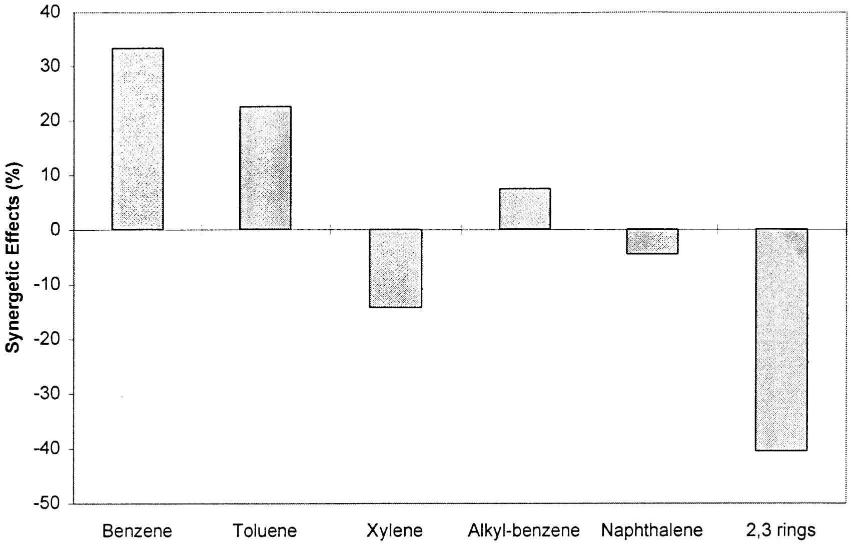

Fig. 6. Synergetic effects for the $> C_6$ compounds obtained in the co-pyrolysis of demineralized Samca coal/PR mixtures: 70/30.

As has been previously stated [32], acid treatment modifies the porous structure derived from coal so that after pyrolysis of a demineralised coal a more porous solid matrix that allows a properly volatile release is obtained. These volatiles can easily undergo gas phase reactions and lead to an increase in the aromatic compounds production and this seems the most convincing explanation for the synergetic effects observed for the demineralised coal mixtures.

4. Conclusions

The influence of coal and mineral matter nature and coal/petroleum residue weight ratio on the synergetic effects observed when coal and petroleum residue is copyrolysed has been studied. It has been shown that for the low-rank coal (Samca coal) an increase of petroleum residue ratio promotes the production of light olefins, disfavouring the production of aromatic compounds. In contrast, for the high rank coal (Figaredo coal), petroleum residue ratio does not influence to a great extent the interactions between PR and coal. In this case, the synergetic trends are similar for mixtures 70/30, 50/50 and 40/60. An increasing in the synergetic effects for the production of light olefins and BTX have been observed after demineralisation of the Samca coal. However, it can not firmly concluded that these high synergetic effects observed after demineralisation were only due to the elimination of mineral matter since the increase observe in both, volatile compounds release and gas phase interactions, might also be a consequence of the acid treatment.

Acknowledgements

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