Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 125–134

STUDY OF SULPHUR IN OXIDISED COALS BY ATMOSPHERIC PRESSURE–TEMPERATURE PROGRAMMED REDUCTION

M. Kozłowski [1*], *R. Pietrzak* [1], *H. Wachowska*[1] *and J. Yperman*[2]

[1]Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[2]Laboratory of Applied Chemistry, IMO, Limburgs Universitair Centrum, B-3590 Diepenbeek, Belgium

(Received June 12, 2003; in revised form September 28, 2003)

Abstract

The influence of oxidation of coal, performed with different oxidising agents, on the sulphur species was studied. Conversions of the sulphur species were investigated by the Atmospheric Pressure–Temperature Programmed Reduction method (AP–TPR). The removal of pyrite proved to be advantageous for AP–TPR analysis. It was found that non-thiophene sulphur species undergo easier oxidation by different agent then thiophenic structures.

Keywords: AP–TPR, coal, oxidation, sulphur

Introduction

The processes of coal oxidation have been for a long time a subject of great interest both from the point of view of research and industrial applications. Especially, the behaviour of coal towards molecular oxygen is a matter of practical importance. It is well-known that nearly all coals, when in contact with the atmosphere, shows signs of weathering, as results of which the calorific values and the coking properties are harmfully affected. A fact of even greater significance is that many coals while stored in air are liable to spontaneous combustion [1].

A particular subject of concern is the influence of oxidising agents on sulphur species in coal, stimulated by the fact of a substantial impact of sulphur on the natural environment [2]. Many thermal methods have been applied to the investigation of coals [3, 4]. Concerning sulphur in coals, it can be analysed using such thermal techniques as temperature-programmed oxidation (TPO, CATPO) [5, 6], temperature-programmed pyrolysis (TPP) [7], flash pyrolysis [8], temperature-programmed reduction (TPR) [9], its atmospheric-pressure (AP–TPR) [10] and high-pressure variants (HP–TPR) [11]. During analysis by AP–TPR, a coal sample is gradually heated

---

[*] Author for correspondence: E-mail: mkozlow@amu.edu.pl

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

in hydrogen atmosphere and H_2S formed in these conditions is quantitatively determined by a detector with an ion-selective electrode. Because the results of the AP–TPR analysis can be disturbed by the presence of the mineral components in the coal, in our earlier work [12] the measurements were made for Radmacher demineralised coal samples [13]. Unfortunately, the process of coal demineralisation by HCl and HF, leading to a considerable decrease in the contents of the ash, does not remove pyrite – a component insoluble in these acids. In the AP–TPR kinetograms the signals assigned to pyrite overlap those corresponding to organic sulphur species, which significantly disturbs the interpretation of results. For this reason, we have decided to perform the study for pyrite-free samples.

Pyrite can be removed by physical or chemical methods, however, the former (e.g. floating in 1.67 specific gravity solution of CsCl [14]) are less effective than the latter. On the other hand, the effective chemical methods always cause some changes in the organic structure of the coal. For instance, pyrite reduction by $LiAlH_4$, $NaBH_4$ or $CrCl_2$ [15–19] leads to some reduction of the coal substance. The oxidation of pyrite (usually by HNO_3) also causes some coal oxidation [20, 21]. In this study we have decided to remove pyrite by HNO_3, as in the studies of the effect of oxidation the use of an oxidation method seemed more reasonable than the reductive one.

The study aims at determining the effect of oxidation of pyrite-free coal on the transformation of sulphur species.

Experimental

The study was performed for five types of coal characterised by different degree of metamorphism and different content of sulphur. The coal samples studied were: Labin (Croatia), Mequinenza (Spain), Czeczot, Siersza and Zofiówka (Poland). The samples were demineralised by HCl and HF [13] and then pyrite was removed by shaking with diluted HNO_3 at room temperature for 48 h [22]. The demineralised samples, additionally devoid of pyrite, were subjected to oxidation using: peroxyacetic acid (PAA) for 6 h at 40°C, 5% HNO_3 at its boiling point for 6 h, and oxygen gas in 0.25 Mol solution of Na_2CO_3 for 6 h at 80°C. The coal samples were also oxidised in dry phase in air at 125°C for 7 days. Full characterisation of the initial coal samples and the products of their oxidation as well as the details of the preparation methods were given in earlier works [12, 23].

Apparatus and experimental procedure of the Atmospheric Pressure–Temperature Programmed Reduction (AP–TPR) are described elsewhere [10]. In each experiment, approximately 40 mg of sample and 60 mg of fumed silica were placed in the reactor under a 50 cm^3 min^{-1} flow of pure hydrogen. A linear temperature programme of 5°C min^{-1} from room temperature up to 1000°C was followed. The formed H_2S gas was potentiometrically detected as S^{2-}. Identification of particular forms of sulphur was made on the basis of the measurements on model compounds [24–27]. The kinetograms obtained are shown in Figs 1–6.

Results and discussion

The data shown in Table 1 indicate that the oxidation of the coals studied by the oxidising agents applied, leads to a decrease of the sulphur content in all samples. This decrease is the greatest when using PAA and HNO_3, whereas the oxidation in the O_2/Na_2CO_3 system or by air is less effective. The oxidation of the samples Labin, Czeczot and Siersza by air in dry phase leads to the appearance of trace amounts of sulphates. As the pyrite free coal samples do not contain inorganic sulphur, the only source of sulphates must be the oxidation of certain organic sulphur species. Most probably, processes of this kind take place also on oxidation in aqueous media, but then the sulphate ions formed are washed out with water.

The values of sulphur recovery in AP–TPR measurements are in general not high. This fact is related to the three factors: the presence of some mineral substances, mainly calcium compounds, which can bind H_2S forming during measurements [28, 29], the presence of sulphur in the form of particularly stable thiophene groups, which are not hydrogenated during the AP–TPR analysis [30] and release of sulphur in the form of compounds other than H_2S undetected by the potentiometric detection system [26, 31, 32]. For the oxidised samples the last process is particularly important as the oxide sulphur species can produce SO_2 and other volatile sulphur species, apart from H_2S, during the AP–TPR analysis [26, 31, 32]. The lowest values of sulphur recovery obtained for the coal samples oxidised by PAA suggest that this oxidising agent is the most effective in conversion of organic sulphur into its different oxide forms.

The temperatures at which particular sulphur species give signals in the AP–TPR kinetograms, obtained for model compounds, are given in [12]. The majority of the kinetograms presented reveal two main broad peaks (Figs 1–6). On the basis of the results obtained for the model compounds, the first of these peaks with a maximum in the range 400–500°C, can be interpreted as produced by superposition of the signals coming from different non-thiophene groups. The other one with a maximum above 600°C can be interpreted as representing thiophene groups.

On the basis of the kinetograms presented in Fig. 1, we can estimate the effect of demineralisation (AP–TPR recovery of demineralised sample=77% [12]) and pyrite removal on particular sulphur species. The demineralisation of Czeczot coal sample by the method of Radmacher and Mohrhauer changes the general shape of the AP–TPR kinetogram only a little. A small widening of the signal is found in the low- as well as in the high-temperature range. This is related to the removal of certain mineral substances (mainly calcium species), which bind H_2S formed during the AP–TPR measurement.

Significant changes in the shape of the AP–TPR kinetogram appear as a result of pyrite removal. The intensity of the signals at 460 and 510°C considerably decreases. According to the results of the study on the model compounds, these signals can be assigned to the reduction of pyrite to troilite [26]. The signal still visible in this range (shoulder near 460°C) after pyrite removal is assigned to the non-thiophene sulphur species, whereas the peak with a maximum at 620°C corresponds to the thiophene structures [12]. The intensity of the latter peak decreases after pyrite removal, however, it is a consequence of a decrease in the sulphur recovery for this sample (Ta-

Table 1 The contents of different forms of sulphur in the coals investigated and sulphur recovery by AP–TPR method (mass%, dry coal)

Coal	Total sulphur	Sulphate sulphur	Pyritic sulphur	Organic sulphur	Sulphur recovery by AP–TPR
Labin					
Raw	10.03	0.02	0.34	9.67	44
Pyrite-free	10.53	0.00	0.00	10.53	62
Oxidised with HNO_3	9.26	0.00	0.00	9.26	63
Oxidised with PAA	8.52	0.00	0.00	8.52	56
Oxidised with O_2/Na_2CO_3	10.08	0.00	0.00	10.08	61
Oxidised with air	9.63	0.02	0.00	9.61	73
Mequinenza					
Raw	9.67	0.81	1.22	7.64	73
Pyrite-free	8.81	0.00	0.00	8.81	75
Oxidised with HNO_3	7.06	0.00	0.00	7.06	68
Oxidised with PAA	7.08	0.00	0.00	7.08	20
Oxidised with O_2/Na_2CO_3	8.78	0.00	0.00	8.78	71
Oxidised with air	8.79	0.00	0.00	8.79	61
Czeczot					
Raw	1.65	0.05	0.64	0.96	87
Pyrite-free	1.03	0.00	0.00	1.03	73
Oxidised with HNO_3	0.95	0.00	0.00	0.95	77
Oxidised with PAA	0.95	0.00	0.00	0.95	45
Oxidised with O_2/Na_2CO_3	0.99	0.00	0.00	0.99	86
Oxidised with air	1.01	0.04	0.00	0.97	69
Siersza					
Raw	2.29	0.37	1.44	0.48	64
Pyrite-free	0.92	0.00	0.00	0.92	65
Oxidised with HNO_3	0.73	0.00	0.00	0.73	61
Oxidised with PAA	0.83	0.00	0.00	0.83	36
Oxidised with O_2/Na_2CO_3	0.86	0.00	0.00	0.86	62
Oxidised with air	0.84	0.04	0.00	0.80	62
Zofiówka					
Raw	0.67	0.01	0.20	0.46	88
Pyrite-free	0.66	0.00	0.00	0.66	58
Oxidised with HNO_3	0.44	0.00	0.00	0.44	73
Oxidised with PAA	0.45	0.00	0.00	0.45	56
Oxidised with O_2/Na_2CO_3	0.46	0.00	0.00	0.46	81
Oxidised with air	0.50	0.00	0.00	0.50	71

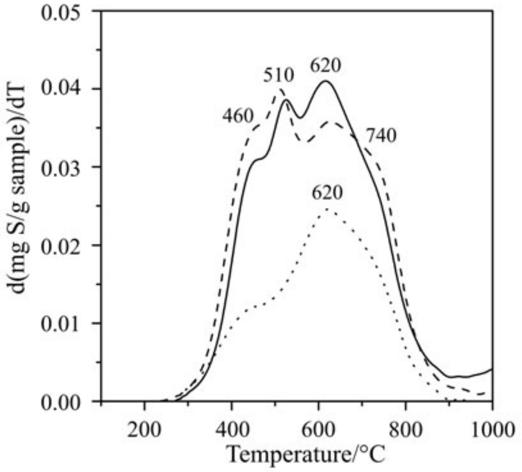

Fig. 1 AP–TPR kinetograms of Czeczot coal: —— – fresh, ----- – demineralised, ····· – pyrite-free

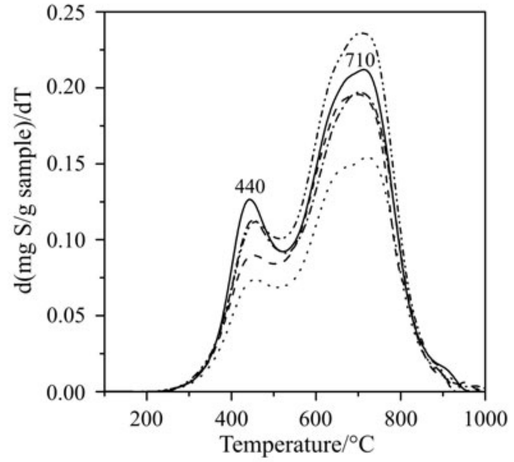

Fig. 2 AP–TPR kinetograms of Labin pyrite-free coal: —— – initial coal, ----- – oxidised with HNO_3, ····· – oxidised with PAA, -·-·-·- – oxidised with O_2/Na_2CO_3, -··-··- – oxidised with air

ble 1). A similar influence of demineralisation and pyrite removal on the AP–TPR kinetograms was noted for the other coal types (results not presented in this paper).

The oxidation of Labin coal (Fig. 2) causes some slight shift of the peak localised originally at 440°C towards higher temperatures, which suggests that the non-thiophene groups like disulphides or dialkyl sulphides are easier to undergo oxidation than alkyl-aryl or diaryl sulphides, which give signals at higher temperatures. The oxidation also causes a decrease of the ratio of intensities of the signals assigned to non-thiophene and thiophene groups. This fact indicates that the non-thiophene sulphur groups are more susceptible to oxidation. These changes are found to be the greatest for the samples oxidised with HNO_3 and air, followed by PAA, while the oxidation in the O_2/Na_2CO_3 system causes smallest changes in the kinetogram, which indicates little effectiveness of this system in oxidation.

The Mequinenza coal sample (Fig. 3) is characterised by a greater contribution of the non-thiophene sulphur groups than Labin (peak at about 400°C). The kinetograms taken for this sample reveal also greater changes caused by particular oxidising agents. Similarly as for Labin coal, the maximum of the peak assigned to non-thiophene groups is shifted towards higher temperatures, but by a much greater value. This observation confirms the conclusion about unequal susceptibility of particular non-thiophene sulphur species towards oxidation in general and towards different oxidation agents. As follows from the kinetograms presented, the most effective oxidising agents are HNO_3 and air, and the most susceptible to oxidation are non-thiophene sulphur groups. The oxidation in the O_2/Na_2CO_3 system causes the smallest shift of the peak originally localised at 400°C and the smallest changes of the ratio of intensities of the signals assigned to non-thiophene and thiophene sulphur, which confirms the small effectiveness of this system. An exceptionally low value of sulphur recovery obtained for the coal oxidised with PAA makes the relevant kinetogram practically impossible for interpretation. On the other hand, this fact indicates a high degree of conversion of the organic sulphur into its oxide forms giving during AP–TPR analysis large amounts of SO_2 (not measured by the used potentiometric detection set-up) apart from H_2S, which leads to a decrease of sulphur recovery.

The content of non-thiophene sulphur in the Czeczot coal sample (Fig. 4) is lower than in the samples of Labin and Mequinenza (the signal at ~450°C). As this form of sulphur has been earlier noted to be the most susceptible for oxidation, the influence of particular processes of oxidation on the shape of the kinetograms is smaller. The

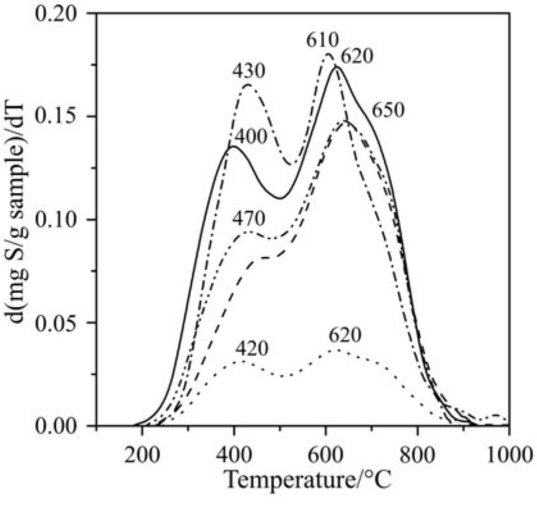

Fig. 3 AP–TPR kinetograms of Mequinenza pyrite-free coal: —— – initial coal, ----- – oxidised with HNO_3, ····· – oxidised with PAA, -·-·-·- – oxidised with O_2/Na_2CO_3, -··-··- – oxidised with air

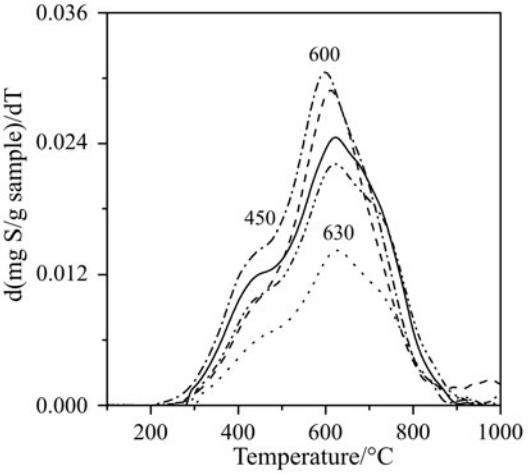

Fig. 4 AP–TPR kinetograms of Czeczot pyrite-free coal: —— – initial coal, ----- – oxidised with HNO_3, ····· – oxidised with PAA, -·-·-·- – oxidised with O_2/Na_2CO_3, -··-··- – oxidised with air

kinetograms for the samples oxidised with different agents have similar shapes and differ only in the intensity, which is a consequence of the differences in sulphur recovery (Table 1). A significant difference can only be noted for the kinetogram of the sample oxidised by HNO_3, in which the shoulder near 450°C is the least pronounced, indicating high effectiveness of this oxidising agent. Similarly as for other types of coal, the signals from the sample oxidised by PAA are the lowest as a consequence of very low sulphur recovery. This observation also proves a high degree of sulphur conversion into different oxide forms. In contrast to the Labin and Mequinenza coals, the oxidation of the Czeczot sample by air was not so effective and only a small intensity lowering over almost the whole temperature range is observed.

The AP–TPR kinetograms shown in Fig. 5 prove that the contribution of the non-thiophene sulphur in Siersza coal is higher than in Czeczot (Fig. 4), but not as high as in Labin and Mequinenza (Figs 2, 3). They also indicate that the least effective is the oxidation in the O_2/Na_2CO_3 system. More effective is the oxidation by air and still more the oxidation by HNO_3. Similarly as for the samples discussed above, the greatest degree of conversion to oxidised forms of sulphur was observed for the sample oxidised by PAA, which is evidenced by low intensity of signals and very low value of sulphur recovery.

The character of the kinetograms of Zofiówka coal (showing the highest degree of coalification among the samples studied) is different (Fig. 6). The main form of sulphur present in this type of coal is the thiophene sulphur (the peak with a maximum at 740°C). Since the shape of the kinetograms is similar and the values of sulphur recovery are much more spread and divers, it is thus difficult to assess the effectiveness of particular oxidising agents for this type of coal. The fact that Zofiówka coal contains mainly thiophene sulphur together with the data shown in Table 1, testifying to a decrease of the sulphur content as a result of all the processes of oxidation, proves that also thiophene sulphur species must be susceptible to oxidation.

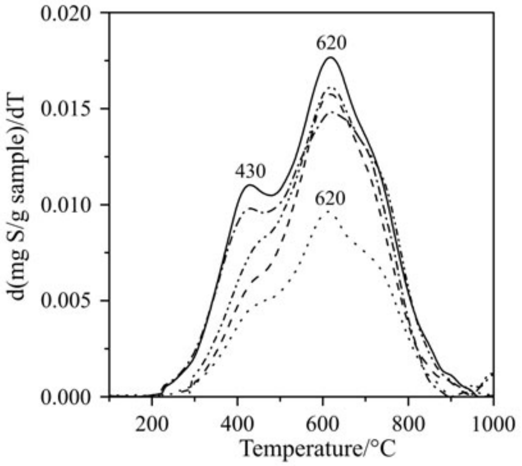

Fig. 5 AP–TPR kinetograms of Siersza pyrite-free coal: —— – initial coal, ----- – oxidised with HNO_3, ····· – oxidised with PAA, -·-·-·- – oxidised with O_2/Na_2CO_3, -··-··- – oxidised with air

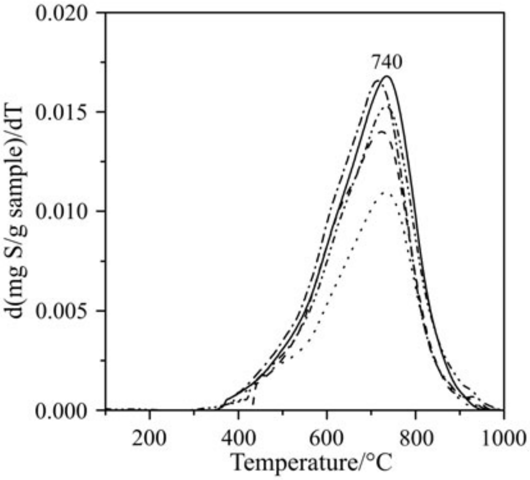

Fig. 6 AP–TPR kinetograms of Zofiówka pyrite-free coal: —— – initial coal, ----- – oxidised with HNO_3, ····· – oxidised with PAA, -·-·-·- – oxidised with O_2/Na_2CO_3, -··-··- – oxidised with air

Further analysis of kinetograms of initial coals (Figs 1–6), points to a reduction in the contribution of non-thiophenic sulphur to total sulphur with increase in coal metamorphism. It was impossible to obtain correct results of non-thiophenic sulphur contributions during AP–TPR studies of pyrite-containing coals, because pyrite-originated signals and signals originated from both non-thiophenic and thiophenic groups partially overlap [12].

Conclusions

The removal of pyrite proved beneficial for interpretation of AP–TPR kinetograms. The pyrite-free coal samples are susceptible for oxidation with the oxidising agents used in this study. The most effective oxidising agents were PAA and HNO_3 (in some cases also air), while the least effective was the oxidation in the O_2/Na_2CO_3 system. The easiest to undergo oxidation are non-thiophene sulphur species and their susceptibility to oxidation by the oxidising agents used is different. Thanks to the removal of pyrite it was possible to show that the thiophene species are also susceptible to oxidation although to a lower degree than the non-thiophene ones. Moreover, the removal of pyrite enabled a determination of the contribution of the non-thiophene sulphur species in the total sulphur content in the samples studied. Their contribution in general decreases with increasing degree of the coal metamorphism.

References

1 D. W. Van Krevelen, Coal: Typology-Chemistry-Physics-Constitution, Elsevier, Amsterdam 1993.
2 M. J. Chadwick, N. H. Highton and N. Lindman (Eds), Environmental impacts of coal mining and utilization, Pergamon Press, Oxford 1987.
3 M. V. Kök, J. Therm. Anal. Cal., 68 (2002) 1061.
4 K. E. Ozbas, M. V. Kök and C. Hicyilmaz, J. Therm. Anal. Cal., 69 (2002) 541.
5 J. P. Boudou, J. Boulègue, L. Maléchaux, M. Nip, J. W. de Leeuw and J. J. Boon, Fuel, 66 (1987) 1558.
6 R. B. LaCount, R. R. Anderson, S. Friedman and B. D. Blaustein, Fuel, 66 (1987) 909.
7 C.-L. Chou, K. C. Hackley and J. Cao, Processing and Utilization of High-Sulfur Coals V, B. K. Parekh and J. G. Groppo (Eds), Elsevier Science Publishers B.V., London 1993, p. 15.
8 W. H. Calkins, Energy Fuels, 1 (1987) 59.
9 A. Attar, Analytical Methods for Coal and Coal Products, Vol. III; C. Karr Jr., (Ed.), Academic Press, New York 1979, p. 585.
10 J. Yperman, I. I. Maes, H. Van den Rul, S. Mullens, J. Van Aelst, D. V. Franco, J. Mullens and L. C. Van Poucke, Analitica Chimica Acta, 395 (1999) 143.
11 S. C. Mitchell, C. E. Snape, R. Garcia, K. Ismail and K. Bartle, Fuel, 73 (1994) 1159.
12 M. Kozłowski, R. Pietrzak, H. Wachowska and J. Yperman, Fuel, 81 (2002) 2397.
13 W. Radmacher and P. Mohrhauer, Brennstoff-Chemie, 37 (1956) 353.
14 S. R. Palmer, E. J. Hippo, M. A. Kruge and J. C. Crelling, Geochemistry of Sulfur in Fossil Fuels, W. L. Orr and C. M. White (Eds), ACS Symposium Series 429, American Chemical Society, Washington DC 1990, Ch. 18.
15 G. Gryglewicz and S. Jasieńko, Fuel, 71 (1992) 1225.
16 D. L. Lawlor, J. I. Fester and W. E. Robinson, Fuel, 42 (1963) 239.
17 W. L. Orr, Geochemistry, 10 (1986) 499.
18 M. M. Vrvic, V. Djordjevic, O. Savkovic, J. Vucetic and D. Vitrovic, Org. Geochem., 13 (1988) 1109.
19 Y. Shi, E. C. Orr, L. Shao and E. M. Eyring, Fuel Process. Technol., 59 (1999) 79.
20 W. H. Calkins, Fuel, 73 (1994) 475.
21 R. M. Davidson, Fuel, 73 (1994) 988.

22 H. Wachowska, M. Kozłowski and M. Pietrowski, Karbo-Energochemia-Ekologia, 41 (1996) 199.

23 R. Pietrzak and H. Wachowska, Fuel, 82 (2003) 705.

24 K. Ismail, S. C. Mitchell, S. D. Brown, C. E. Snape, A. C. Buchanan, P. F. Britt, D. V. Franco, I. I. Maes and J. Yperman, Energy Fuels, 9 (1995) 707.

25 I. I. Maes, J. Yperman, H. Van den Rul, D. V. Franco, J. Mullens, L. C. Van Poucke, G. Gryglewicz and P. Wilk, Energy Fuels, 9 (1995) 950.

26 J. Van Aelst, J. Yperman, D. V. Franco, L. C. Van Poucke, A. C. Buchanan III and P. F. Britt, Energy Fuels, 14 (2000) 1002.

27 P. Rutkowski, S. Mullens, J. Yperman and G. Gryglewicz, Fuel Process. Technol., 76 (2002) 121.

28 I. I. Maes, G. Gryglewicz, J. Yperman, D.V. Franco, J. Mullens and L. C. Van Poucke, Fuel, 76 (1997) 143.

29 M. Kozłowski, H. Wachowska, J. Yperman, D. V. Franco, J. Mullens and L. C. Van Poucke, Energy Fuels, 12 (1998) 1142.

30 B. B. Majchrowicz, J. Yperman, J. Mullens and L. C. Van Poucke, Analytical Chemistry, 63 (1991) 760.

31 S. Mullens, J. Yperman, T. O. Bozdemir, T. Durusoy, Y. Yürüm, D. V. Franco, J. Mullens and L. C. Van Poucke, Proceedings of the 10th ICCS 1999, Vol. II, p. 1135.

32 S. Mullens, J. Yperman, G. Reggers, R. Carleer, A. C. Buchanan III, P. F. Britt, P. Rutkowski and G. Gryglewicz, Submitted for publication.