PN-ABP-890

8.344

FINAL REPORT
Covering Period: 08.12.1988- 12.11.1991

Submitted to the Office of the Science Advisor
U.S. Agency for International Development

UPGRADING LIGNITES VIA THERMAL REDUCTION WITH COKE-OVEN GASE FOR POSSIBLE UTILIZATION IN METALLURGICAL COKE PRODUCTION

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Project Number : 8.344
Grant Number: DPE-5542-G-SS-8031-00

A.I.D Grant Project Officer: Dr.Alberto Sabadell

Project Duration : 08.12.1988-12.11.1991

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EXECUTIVE SUMMARY

The aim of this research project was to develop a process for upgrading the rheological properties of low rank coals and lignites for the purpose of utilizing these lignites in metallurgical coke production by blending the processed lignites with coking coals in significant proportions

Coke-oven gas, a by-product of steel industry has been used as the reducing processing gas for upgrading the lignites, for the sake of the technical and economical feasibility aspects of the process.

Çukurova University supplying the major executing research group leading both in process developing and analytical evaluation experiments, ISDEMIR Iron & Steel Works, Co supplying the laboratory area in the plant, the coke-oven gas for processing and some machine-shop facilities and the Colorado State University supplying the solid-state NMR facilities for analytical evaluation of processed lignites, collaborated efficiently and successfully throughout the entire project.

The project has achieved its scientific goal such that at the bench-scale level, a process has been developed by which the low-rank coals and lignites could be upgraded significantly and utilized in metallurgical coke production. It has also been shown that the developed process could be economically feasible. Steel plants based on conventional blast-furnace technology and already having coke production plants can add this technology without any changes in their existing coke-battery system.

In general low-rank coals and lignites are being utilized in power plants and creating extensive environmental pollution. The process developed in this project also furnishes an alternative for utilizing these low-rank fossil fuels.

The research scientists of Çukurova University, ISDEMIR Iron & Steel Works, Co and Colorado State University had a strong scientific interaction throughout the project activities and developed their knowledge and skills further regarding the theoretical and practical aspects of various scientific topics involved in this project. The Çukurova University Group also had the chance of strengthening their laboratory capacity by making use of the AID Grant.

OBJECTIVES

Metallurgical coke which is being utilized in blast furnaces of steel industry can only be produced from certain coking coals. The carbon content of these coals, on dry, ash-free basis, fall in the range 84-91 % by weight and these coals also fulfil certain physical and chemical property requirements for producing good quality metallurgical cokes. Sub-bituminous coals and lignites cannot be utilized in metallurgical coke production in their original forms. Thus, countries like Turkey lacking enough coking coal reserves are trying to find alternative processes for utilizing their domestic low-rank coals in metallurgical coke production.

Previous research work has shown that treatment of non-coking coals and lignites with hydrogen and/or methane under certain pressure and temperature conditions improves their coking properties (1-5). Similar results have been obtained from carbonmonoxide/water treatment of non-coking coals and lignites (6-8)

In this work, the main aim was to develop a process for uprading the rheological properties of low-rank coals and lignites for the purpose of utilizing these solid fuels in metallurgical coke production by blending the processed solids with coking coals in significant proportions. In order to develop a technically and economically feasible process, coke-oven gas, a by-product of coke (steel) plants, has been used for processing the low-rank solid fuels.The main active components of this gas mixture were hydrogen, methane and carbonmonoxide with the percentages 60 ± 1 %, 22 ± 1 % and 7.0± 0.5 % , respectively. The combined effect of these gases in such a mixture on upgrading lignites has not been investigated previously.

It is expected that the information generated in this project could be of immediate interest and benefit to the steel industries of developing countries in which conventional blast- furnace technology is being used.

MATERIALS AND METHODS

Lignites and Processing Gases

Three low-rank coals, a sub-bituminous coal and two lignites were used throughout the processing experiments. The sub-bituminous coal, Tunçbilek which has been denoted by T in this report and the two lignites, Çan and Soma, denoted with C and S, respectively were all from the western Anatolia region of Turkey. Proximate and ultimate analysis data of these coals are given in Table 3.

The coke-oven gas from ISDEMIR coke plant was used in processing the coals after having been cleaned by using filters. The exact composition of this gas is given in Table 4.

Processing Experiments

The three low-rank coals were processed by using coke-oven gas in two different reactor systems. The first reactor was a 2 L inner volume, mechanically stirred autoclave. Small amounts of water were charged into the autoclave in some experiments to balance the desired final operating pressure. In a typical experiment, after charging the lignite, the air inside the autoclave was swept successively with nitrogen and coke-oven gas and an initial pressure of 6 MPa (or other calculated pressures) coke-oven gas at ambient temperature (23 ± 2°C) was maintained. The range of operating temperatures and pressures are given in Tables 1 and 2. The experiments carried out in this system are called "Non-Circulating Gas Batch-Type Processing" throughout this report.

The second reactor system was composed of a main tubular reactor of 7.4 cm internal diameter and 1.5 m internal height, to which high-pressure filters and pre-heating sytems were coupled. The reactor had metal discs of 0.5μm porosity in the entrance and exit parts which hold the lignite particles inside but allows the processing gas pass through. A dry test meter was installed in the exit part of the system for measuring the volume of the gas passing through the system. The coke-oven gas was pressurized by using a three-stage high-pressure compressor. The experiments carried out in this system were called "Circulating- Gas Batch-Type Processing" in this Report.

Physical and Chemical Analysis and Tests

Proximate (ash, volatile matter) analysis of untreated and treated coals were done according to the standart ISO methods. LECO instruments were used for the C, H, N, S determinations and oxygen was calculated by difference.

Gas analysis were done by a Shimadzu gas chromatograph equipped with a thermal conductivity detector. A single column (Carbosive S-II) was used to analyze the gases given in Table 4.

The treated lignite samples, following a sample preparation of embedding in an epoxy resin and polishing, were investigated by using a polarized reflected-light microscope.

Dilatation tests of treated lignites blended with coking coals were done by using a Ruhr dilatometer with a heating rate of $3.0 \pm 0,.1$ °C/min.

The liquid products produced during processing of lignites were extracted with n-hexane and analysed by a Hewlett-Packard Gas chromatograph-Mass Selective Detector system.

The untreated and treated lignites were also investigated by solid-state ^{13}C CP/MAS NMR by using a home-built NMR spectrometer in the Regional NMR Centre of Colorado State University.The spectra are recorded at 15 MHz with a bullet rotor operating at about 2.5 kHz. This spinning speed places the first-order spinning side bands at about 290 to 300 ppm and about –20 to -30 ppm in the spectra, conveniently outside the usual range of diamagnetic species found in coals. Hence, sideband intensity has been taken into account in determining f_a' values (vide infra). Hartmann-Hahn match conditions involved radio frequency field strengths of about 12 Gauss and 48 Gauss for ^{1}H and ^{13}C, respectively. A contact time of 1ms and repeat time of 0.7 s were employed; these parameters have been shown in previous work to yield representative ^{13}C CP/MAS result s(10,11)

Coke Production and Related Analysis and Tests

Cokes were obtained in a laboratory-scale vertical tube furnace of 5 cm internal diameter. In a typical coking experiment, 400 g of coal was charged to the tube and heated with a rate of 3°C/min to 1100°C and kept at this temperature for 2.5 hr. Nitrogen gas was passed with a very slow flow rate through the tube throughout the coking and cooling periods.

The tensile-strength tests of the cokes produced were carried out according to the method used by Patrick et al (9).

The cokes and semi-cokes produced from the blends of treated lignites and coking coals were also investigated by using polarized reflected-light microscope as described before.

RESULTS AND DISCUSSION

The processing experiments were carried out in three major groups. The first group of experiments were done by using Tunçbilek coal only in the non-circulating gas mode in order to determine the optimum processing conditions at this mode of operation. The second group of experiments were also carried out in the same mode of operation by using Tunçbilek coal and Çan and Soma lignites. A thorough study with all the physical and chemical methods described in Materials and Methods section were realized in this part of the work. The third group of processing experiments were done in the circulating gas mode of operation in the second reactor system. This group of experiments at bench -scale level were designed to test the validity of the process at industrial level.

Optimization of Reaction Conditions in Non-Circulating Gas Mode of Operation

The affect of four different process parameters, namely particle size of coal, temperature of the reaction system, pressure of the reaction system and the residence time of reaction were investigated by using Tunçbilek coal. The reactions were carried out in the 2 L autoclave system.

Table 1 summarizes the operational data of the pocessing experiments. The processed Tunçbilek coal samples were systematically investigated by the polarized reflected-light microscope in order to determine the development of anisotropic structures which were a direct measure of upgrading the rheological properties. At this mode of operation, it was determined that the particle size of -0,25 mm, the operating pressure of 15 MPa, the residence time of 90 min. would be optimum parameters. Temperature of the reaction medium was the most important parameter and it was decided that more thorough studies at different temperatures should be conducted by using the other lignites in the second group of processing experiments.

Non-Circulating Gas Mode Operations and Related Analysis

In this group of experiments Tunçbilek coal and Çan and Soma lignites were processed in the autoclave with coke-oven gas at three different temperatures while the other process parameters were kept constant. The details of the operational data are given in Table 2. Each coal has been subjected to processing at the same operational parameters twice and one of the processed sample was extracted with n-hexane and the other wasn't. Those solids which had been extracted were coded with E and the non-extracted ones with N following the initial letter designating the original coal. The samples which had not been extracted were altogether called Group I samples and those which had been extracted were called Group II samples in the related tables.

Table 3 gives the proximate and ultimate analysis results of the unprocessed and processed Tunçbilek coal and the Çan and Soma lignites under non-circulating gas mode of operation. There are pronounced decreases in oxygen contents of these solid fuels following the thermal treatment in the autoclave in the presence of coke-oven gas. It seems that the main oxygen removal from these solid structures takes place at or before 350°C under the stated process conditions. One notes that the oxygen content of processed lignite samples extracted with n-hexane are relatively higher than the corresponding samples which are not extracted. This means that, following processing with coke-oven gas, most of the remaining oxygen functional groups probably constitute an integrated part of the main macromolecular structure rather that being in the extractable material. After processing in the autoclave, slight decreases in sulphur contents and slight increases in hydrogen contents of the solid samples are noted whereas increases in carbon contents are relatively prominent. One also notes that the hydrogen contents of processed solid samples extracted with n-hexane are relatively lower than the corresponding processed solid samples which are not extracted, indicating that n-hexane extracts are rich in aliphatic structures as expected. These n-hexane extracts, which represents about 3 % of the daf coal are composed mainly of straight-chain alkanes. GC-MS analysis results of these paraffinic material obtained from processed Çan and Soma lignites are given in Figures 1 and 2. The concentration of aromatic compounds present in these extracts are very low and are mainly composed of methyl-substituted biphenyls, dibenzyls, naphthalenes and florenes.

Investigation of the CP-MAS ^{13}C NMR spectra of untreated and treated coal samples gave the following information. Carboxyl and/or carbonyl group absorptions (~ 175 ppm) almost disappeared following the treatment at 380°C in all three coals studied. Oxygen substituted phenolic and/or etheric aromatic carbon absorption (~ 155 ppm) decreased following the treatment at 380°C but complete disappearance took place after the treatment of 420 °C. Following the treatments at 380°C and 420 °C, absorptions due to long-chain and/or branched-chain aliphatics decreased relatively more than the adsorptions due to methyl and other short and straight-chain aliphatics. These decreases were much more prominent in n-hexane extracted solid samples indicating that most of these aliphatic structures were extractable. Indeed, GC-MS analysis, as stated previously, gave the detailed composition of the n-hexane extracts which were mainly straight-chain alkanes.

The apparent aromaticity values (f_a') of all three coals increased dramatically following the treatments with coke-oven gas. These f_a' values which were calculated by using the integration values of aromatic and aliphatic regions in CP-MAS ^{13}C NMR spectra are given in Table 3.

The composition of the coke-oven gas used in processing the lignites and the compositions of the gases in the autoclave after the treatments are given in Table 4. There are relatively significant increases in methane and carbondioxide contents after the treatment of lignites in the autoclave. The carbondioxide concentration reaches approximately to a steady state around the treatment temperature of 350°C which is in agreement with the oxygen values determined for the processed solid samples and with the CP-MAS ^{13}C NMR observations for the same samples. Methane concentration continues to increase at other operating temperatures, namely at 380°C and at 420°C which is also consistent with the elemental analysis and CP-MAS ^{13}C NMR results. Hydrogen concentration decreases due to the reactions with the lignite structures and this decrease continues as the operating temperature in the autoclave is increased.

The details of the optical textures observed by using a polarized reflected light microscope are summarized in Table 5. Some representative optical micrographs are also given in Figures 3,4 and 5. The formation of very small mesophase structures are detected in Tunçbilek and Çan lignites processed at 350°C whereas Soma lignite processed at this temperature is completely isotropic . The first two lignites have more developed anisotropic textures when processed at 380°C whereas in Soma lignite processed at this temperature, formation of very small anisotropic structures are observed. All three lignites processed at 420°C have fused masses with various developed mosaic textures. The semicokes obtained at 550°C from the processed lignites show various mosaic, flow and domain anisotropy as the abundant textures. It should be noted that the optical textures of the semicokes obtained from the unprocessed lignites are completely isotropic.

The unprocessed and processed lignite samples are blended with a coking coal in two different proportions, namely 15 % and 25 % by weight and the blends are subjected to dilatation tests by using a Ruhr dilatometer. Tables 6 and 7 summarize these dilatation test results. The coking coals used for blending with lignites (CC1 and CC2) have high dilatation characteristics, but when these coals are blended with unprocessed lignites, the plasticity and the dilatation suddenly drop. It is observed that plasticity and dilatation characteristics are much higher when the same coking coals are blended with the processed lignites in the same ratios. All these dilatation data given in Tables 6 and 7 are strong indications for the development of rheological properties of lignites after being processed with the coke-oven gas. It seems that for Tunçbilek and Çan lignites, processing with coke-oven gas at 380°C gives the highest dilatations whereas for Soma lignite processing at temperatures above 380°C is necessary to improve the dilatation characteristics.

Table 7 also gives the tensile strengths of cokes produced by using the blends of a coking coal with the unprocessed and processed lignites. These data clearly show that Tunçbilek and Çan lignites after being processed with the coke-oven gas even at 350°C can be blended with coking coals upto

25 % by weight to produce high - strength cokes.Soma lignite, as also seen from various other experimental data was not extensively upgraded and it can only be possible to blend the processed Soma lignite at 380°C with a coking coal with a percentage of 10-15 for obtaining cokes of enough strength for blast-furnace operations .

Circulating Gas Batch - Type Processing

This part of the work was a bench - scale level development of the coke - oven gas treatment of lignites with continuous gas circulation through the reactor system described previously. Since this reactor system was a small - scale imitation of the probable industrial scale processing system, moderate operating pressures (3.5 - 10.5 MPa) were targeted because of the cost of investment and ease of operation.

The important difference of this system from the autoclave was the gas circulation and therefore the availability of higher coke - oven gas amounts per unit weight of lignite being processed. Also the modes of mixing of the lignite particles during the process were different. The effect of variation of the flow rate of the coke - oven gas, the effect of the variation of gas pressure and the effect of the variation of the operation temperature were investigated while the particle size of the lignites (- 0.25 mm) and the reaction duration (1 hour) were kept constant in this part of the work.

Table 8 summarizes the operational data of the circulating - gas mode of the processing experiments.The results of the polarized - reflected light microscopic investigations and the results of the tensile - strength tests that are applied to the cokes obtained from the 25 % blend of treated lignites with the coking coal CC2 are also summarized in this Table. The disadvantage of the low operational pressures are compensated by the relatively high amounts of processing gas as can be calculated from the flow rates of the coke - oven gas.

In this circulating - gas mode of processing, promising results are obtained with Tunçbilek coal and Çan lignite even at 3.5 MPa operating pressures if the flow rate of the gas is sufficiently high (~30 L/min) and the operation temperature is around 380 ^{0}C. The results are better at high operating pressures and best upgrading is obtained at 10.5 MPa for both Tunçbilek coal and Çan lignite. Soma lignite, similar to the results obtained in the first part of the work, didn't show up improvements at low operating pressures or temperatures. In this lignite, upgrading is only observed at severe operating conditions.

Techno - Economic Analysis

A process flow diagram (PFD) is shown in Figure 6. Major unit operations are grinding of the lignite, feeding through a lock hopper system which is well established in the coal gasification industry, a battery of reactors operating in a sequential batch mode, the gas purification and the compression section.

The reactors are considered to operate at a nominal temperature of 350 - 380 ^{0}C and at a pressure of 3.5 MPa. The batch cycle is to be of 60 min and incoming gas velocity (flow rate divided by internal area of reactor at temperature and pressure conditions of the reactor) is to be maintained at just below the minimum fluidization velocity.

Each reactor will have the following characteristics:

* diameter (internal) = 1.25 m
* height = 16 m
* zone occupied by lignite ~ bottom half
* charge of lignite ~10 tonnes per batch
* treatment time ~1 hr
* discharge time ~0.25 hr
* charging time ~0.25 hr
* total batch cycle ~1.50 hr

The treated (and anisotropic) lignite will be removed from the reactor by a blow - out through the cyclone separators into a receiver quencher from where it will be depressurized and recovered. Alternatively, the treated lignite can be cooled to <300 ^{0}C while staying in the reactors and discharged via a reverse blow or any other appropriate approach.

A battery of 4 reactors will treat :

$$\frac{10}{1.5}\,\frac{\text{tonnes raw lignite}}{\text{hr * reactor}} * 0.7\,\frac{\text{dry lignite}}{\text{raw lignite}} * 24\,\frac{\text{hr}}{\text{day}} * 4 \text{ reactors} =$$

$$448\,\frac{\text{tonnes dry lignite}}{\text{day}}$$

and produce about :

$$0.7 * \frac{\text{anisotropic lignite}}{\text{dry lignite}} * 448\,\frac{\text{tonnes dry lignite}}{\text{day}} =$$

$$314\,\frac{\text{tonnes anisotropic lignite}}{\text{day}}$$

Should such a system be developed and installed in USA the following budgetary cost should be contemplated :

Process cost estimates

Item	Estimated Cost ($US, 1993)
Grinding system with sieves and recycle Specs.: 500 tonnes/day <0.5 mm particles 4 grinders	800,000
Hopper system: 2 batteries of (installed) 2 hoppers each	1,200,000

Reactors (x4) as specified above and lined with refractory material. Heating will be provided by the incoming gas	1,600,000
Particule separators : a series of two cyclones per reactor	1,280,000
Pressure relief values	160,000
Receiver / Quenching vessels : One per reactor	640,000
Coke - oven gas : purification / compressors (x2)	960,000
Basic equipment :	6,640,000
Instrumentation	725,000
Peripherals and inter connecting equipment	1,085,000
Total equipment	8,450,000

The total investment cost will include :

Total equipment	8,450,000
Process engineering cost	1,810,000
Civil engineering cost	1,448,000
Total investment : (budgetary estimate having a -20/+40 accuracy)	11,708,000

Assuming an amortization plan of 15 years and a long term interest of 12 % per year, the fixed processing costs over a 15 year period will be :

$$11{,}708{,}000 \left(1 + \frac{120}{15} * 0.12 \right) = 22{,}947{,}680 \text{ USD}$$

The fixed processing cost per tonne of produced anisotropic lignite will be, assuming 330 days of operation per year:

$$\frac{22{,}947{,}680}{15} \frac{\text{USD}}{\text{year}} * \frac{1 \text{ year}}{330 \text{ days}} * \frac{1 \text{ day}}{314 \text{ tonnes anisotropic lignite}} = 14.8 \frac{\text{USD}}{\text{tonne anisotropic lignite}}$$

To this fixed processing costs, the following variable processing costs must be added:

-raw material
-labor and administration
-energy
-Utilities
-Maintenance
-coke - oven gas
-taxes
-interests on working capital

Since these variable costs are specific to a given location / country, we have not included them in our estimation. A rapid order - of - magnitude estimate of the variable costs can be done by multiplying the fixed costs by 2 based on similar processes in the chemical industry. Thus :

Total cost per tonne of anisotropic lignite	=	Fixed processing costs per tonne	+	variable processing costs per tonne	=	44.4 USD/tonne

The anisotropic lignite thus produced is then blended with other coking coals to yield the appropriate coke for the metallurgical operation. The percentage of anisotropic lignite used will replace an equivalent amount of coking coal whose current price (Fall 1993) ranges between 50 - 60 USD / tonne.

The economic strategy of upgrading the lignite is thus feasible based on the estimations presented above.

IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

The research scientists of Çukurova University, ISDEMIR Iron & Steel Works, Co and Colorado State University had a strong scientific interaction throughout the project activities and developed their knowledge and skills further regarding the theoretical and practical aspects of various scientific topics involved in this project.

The Çukurova University Group also had the chance of strengthening their laboratory capacity by making use of the AID Grant. A gas chromatograph - mass spectrometer analysis system was bought and used throughout the project.

The process developed at the bench - scale level seems to be promising. Therefore, the Çukurova University group will propose a collaborated pilot - plant study to ISDEMIR. If positive progress can be developed on this track, AID will be informed and chances and facilities to collaborate with a US company specialized on similar process and technologies will be sought.

PROJECT ACTIVITIES AND OUTPUTS

Project Visits and Meetings Attended

Dr. Oktay Erbatur - June 29, 1989; AID/ Washington

Dr. O. Erbatur visited AID/Science (Dr. Alberto Sabadell) for one day to initiate the AID Grant payments and activities when he was in Penn State/University Park through another project.

Dr. Oktay Erbatur - February 3-21, 1990; CSU/Fort Collins, PennState/University Park, AID/Washington
CSU: Meetings with Prof. Gary E. Maciel and taking part in ^{13}C NMR spectroscopic analysis.
PennState: Meeting with Dr. Harold H. Schobert for discussing lignite processing experiments.
AID: Dr. O. Erbatur gave a seminer to a group in AID including Dr. A. Sabadell about the initial results of the research going on in the project.

Dr. Oktay Erbatur & Dr. Gaye Erbatur - September 5-7, 1990; Cambridge/U.K. Attendance to a Conference: "Coal Structure and Reactivity". A paper on project activities has been submitted (ref. publications)

Dr. Gary E. Maciel - September 8-16, 1990; Adana/Turkey. Meetings with Dr. O. Erbatur and Dr. G. Erbatur

Dr. Oktay Erbatur - December 12-28, 1990; CSU/Fort Collins. Meetings with Prof. Gary E. Maciel and taking part in ^{13}C NMR spectroscopic investigations

Dr. Oktay Erbatur & Dr. Gaye Erbatur - April 2-5, 1991 Cyprus. Attendance to a Conference: "Chem'91":A paper on project activities has been submitted (ref. publications)

Dr. Gaye Erbatur - June 27-July 14; CSU/Fort Collins. Meetings with Prof. Gary E. Maciel and taking part in ^{13}C NMR spectroscopic investigations.

Publications

The following has been published and one paper covering ^{13}C NMR investigations and the circulating - gas mode of processing the lignites is under preparation.

O. Erbatur, L.Artok and G. Erbatur, "Upgrading lignites via thermal reduction with coke - oven gas", Coal Structure and Reactivity, Cambridge, 1990, p.115

O. Erbatur, L. Artok, A. Çoban and G. Erbatur, "Upgrading lignites via thermal reduction with coke - oven gas", Fuel, 1991, 70, 1476

O. Erbatur, L. Artok and G. Erbatur, "Upgrading lignites via thermal hydrogenation", Proc. National Congress Chem'91, Gazimagosa/Cyprus,1991, p.391

O. Erbatur, "Investigation of coals and coal products via Nuclear Magnetic Resonance", Invited lecture in Coal Congress, Didim/Turkey, 1991,pp. 423-440

G. Maciel and O. Erbatur, "NMR Characterization of Solid Fossil Fuels; Coal and Oil Shale", NMR in Modern Technology (Ed. Maciel, G.E.), In press. Submitted in NATO ASI, Sarigerme/Turkey, 1992.

CONCLUSION

The project has achieved its scientific goal such that at the bench - scale level, a process has been developed by which the low - rank coals and lignites could be upgraded significantly and utilized in metallurgical coke production. It has also been shown that the developed process could be economically feasible. Steel plants based on conventional blast - furnace technology and already having coke production plants can add this technology without any changes in their existing coke - battery system.

ACKNOWLEDGEMENT

On behalf of the research groups who had collaborated in this Project, I would like to express our gratitudes to the "Office of the Science Advisor / U.S. Agency for International Development" for the generous support given from "Program in Science and Technology Cooperation" under Grant No. DPE-5542-G-SS-8031-00.

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12. O.Erbatur, L.Artok, A.Çoban, and G.Erbatur, Fuel, 1991,70,1476

APPENDIX 1

Table 1 Operational data of the processing experiments for optimization of the reaction conditions*

Sample Code	Particle size (mm)	T_{op} (°C)	P_{op} (MPa)	Residence time (min)
TS1	-1.00	380± 5	15.0 ± 0.3	90
TS2	-0.50	380 ± 5	15.0 ± 0.3	90
TS3	-0.25	380 ± 5	15.0 ± 0.3	90
TS4	-0.15	380 ± 5	15.0 ± 0.3	90
TT1	-0.25	350 ± 3	15.1 ± 0.2	90
TT2	-0.25	380 ± 5	15.1 ± 0.2	90
TT3	-0.25	400 ± 5	15.1 ± 0.2	90
TT4	-0.25	420 ± 6	15.1 ± 0.2	90
TP1	-0.25	380 ± 5	10.2 ± 0.2	90
TP2	-0.25	380 ± 5	15.3 ± 0.3	90
TP3	-0.25	380 ± 5	18.7 ± 0.2	90
TP4	-0.25	380 ± 5	21.4 ± 0.3	90
TR1	-0.25	380 ± 5	15.2 ± 0.2	30
TR2	-0.25	380 ± 5	15.2 ± 0.2	60
TR3	-0.25	380 ± 5	15.2 ± 0.2	90
TR4	-0.25	380 ± 5	15.2 ± 0.2	120

* In sample codes the first letter, T symbollizes the Tunçbilek sub-bituminous coal, the second letters describe : S-particle-size variation, T-temperature variation, P-pressure variation and R-residence-time variation

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Tablo 2 Operational data of the processing experiments carried out at varying temperatures by using Tunçbilek coal and Çan and Soma lignites

Code	Wt_L (g)	Wt_w (g)	P_i(MPa)	T_{op} (°C)	P_{op} (MPA)
TN1	70	10	6.08	351± 3	14.49 ± 0.20
TN2	70	5	6.08	380 ± 2	14.29 ± 0.10
TN3	70	-	6.08	420 ± 2	14.59 ± 0.20
TE1	200	-	6.08	352 ± 6	14.86 ± 0.24
TE2	200	-	6.08	377 ± 5	15.12 ± 0.13
TE3	200	-	6.08	421 ± 2	15.85 ± 0.20
CN1	70	10	6.08	351 ± 2	14.79 ± 0.20
CN2	70	5	6.08	381 ± 1	14.19 ± 0.10
CN3	70	-	6.08	420 ± 2	14.08 ± 0.10
CE1	200	-	6.08	352 ± 3	13.52 ± 0.33
CE2	200	-	6.08	381 ± 2	14.40 ± 0.03
CE3	200	-	6.08	421 ± 2	15.48 ± 0.17
SN1	70	10	6.08	351 ± 2	15.00 ± 0.2
SN2	70	5	6.08	380 ± 1	14.89 ± 0.10
SN3	70	-	6.08	420 ± 1	15.30 ± 0.10
SE1	200	-	6.08	351 ± 2	15.98 ± 0.07
SE2	200	-	6.08	381 ± 2	17.00 ± 0.04
SE3	200	-	6.08	421 ± 3	17.02 ± 0.12

Wt_L : Weight of lignite charged into the reactor; Wt_w : Weight of water charged into the reactor;
P_i : Pressure of coke-oven gas charged into the reactor at ambient (23 ± 2 °C) temperature;
T_{op} : Operation temperature; P_{op}: Pressure in the reactor at T_{op}

Table 3 : Proximate and ultimate analysis data and the apparent aromaticities (f_a')

Code	Ash	V.M.	C	H	N	S	O	f_a'
T	11.8	45.2	75.7	5.3	2.1	3.2	13.7	0.65
TN1	12.0	39.2	83.5	5.8	3.3	2.3	5.1	0.74
TN2	13.2	33.4	86.8	6.1	3.3	2.4	1.4	0.78
TN3	16.0	22.3	87.3	6.1	3.3	2.6	0.7	0.82
TE1	14.3	30.6	83.3	5.1	3.7	3.1	4.8	0.74
TE2	15.3	23.6	86.5	4.2	3.9	2.8	2.6	0.80
TE3	17.6	12.8	87.6	3.6	3.8	3.2	1.8	0.84
C	17.3	47.4	71.8	5.5	1.3	5.1	16.3	0.64
CN1	22.0	42.1	84.0	5.4	2.3	4.0	4.3	0.70
CN2	23.1	32.9	86.1	6.2	2.2	3.5	2.0	0.82
CN3	23.0	25.3	86.1	6.2	2.3	3.6	1.8	0.84
CE1	21.7	38.5	82.0	5.1	2.5	3.6	6.7	0.71
CE2	25.8	28.4	85.4	4.6	2.8	4.1	3.1	0.83
CE3	26.6	23.5	86.9	4.2	2.6	4.0	2.3	0.85
S	17.1	49.4	71.2	5.5	0.8	1.3	21.8	0.56
SN1	19.7	41.6	85.1	5.7	1.7	1.0	6.5	0.72
SN2	23.0	34.8	87.4	5.3	1.7	0.9	4.7	0.78
SN3	25.2	28.6	89.8	5.9	1.8	1.2	1.7	0.81
SE1	22.6	38.5	84.8	5.4	2.0	1.2	6.6	0.72
SE2	24.9	34.0	86.8	5.0	2.0	1.1	5.1	0.78
SE3	25.4	28.1	87.7	4.8	2.2	1.1	4.2	0.85

The values given are in Wt %; ash on dry basis; the rest are on dry, ash-free basis; oxygen values are by difference. f_a' values are calculated by using the integration values from CP-MAS ^{13}C NMR spectra.

Table 4 Gas compositions after thermal treatment of lignites in the presence of coke-oven gas

Code	H_2	O_2	N_2	CO	CH_4	CO_2	C_2H_4	C_2H_6
Coke-oven gas	60.3	0.5	5.1	7.6	22.3	1.7	1.9	0.6
TN1	54.3	0.4	6.2	7.3	25.2	3.8	1.4	1.4
TN2	51.7	0.1	5.6	7.2	27.9	4.2	1.1	2.2
TN3	47.6	0.2	7.2	7.3	29.6	4.5	0.5	3.1
TE1	44.8	0.3	6.9	5.9	30.1	8.5	0.5	3.0
TE2	38.8	0.2	6.8	4.7	36.0	8.8	0.3	4.4
TE3	29.5	0.1	7.0	4.4	43.6	9.1	0.0	6.3
CN1	53.2	0.3	5.8	6.6	26.1	5.3	1.0	1.7
CN2	51.3	0.2	6.0	6.9	27.4	5.4	1.0	1.8
CN3	48.8	0.3	6.2	6.8	29.2	5.4	0.5	2.8
CE1	42.1	0.2	6.6	3.4	33.1	11.4	0.2	3.0
CE2	37.6	0.3	6.9	2.7	35.9	12.4	0.1	4.1
CE3	30.1	0.2	6.4	1.8	41.5	13.9	0.0	6.1
SN1	56.2	0.3	6.1	6.0	23.7	5.8	0.5	1.4
SN2	54.8	0.3	5.5	6.0	25.4	6.0	0.1	1.9
SN3	51.0	0.4	5.7	5.7	28.1	6.4	0.0	2.7
SE1	51.5	0.2	4.5	3.7	27.4	10.7	0.0	2.0
SE2	40.2	0.2	4.8	2.4	35.4	13.0	0.0	4.0
SE3	39.9	0.2	5.8	2.9	35.5	12.3	0.0	3.4

Values are in mol %

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Table 5 Interpretation of the optical micrographs of the processed lignites and of of the corresponding semicokes (SC) obtained at 550 °C

Sample code	Optical micrograph interpretation
TE1	Small mesophase structures in the isotrope body
TE2	Mosaic textures and other mesophase structures
TE3	Mm > Mc, Mf
TE1SC	Mf > Mm >FD. SD
TE2SC	Mf > MC > Mm, SD
TE3SC	Mm > Mc > Mf,SD
CE1	Small mesophase structures in the isotrope body
CE2	Mosaic textures and other mesophase sutructures
CE3	Mf > Mm
CE1SC	Mf > Mm > SD, I
CE2SC	MC > SD, Mm > Mf
CE3SC	MC > SD, Mm > Mf
SE1	Isotrope only
SE2	Small mesophase structures in the isotrope body
SE3	Mf > Mm, FD, SD
SE1SC	I > Mm, Mf > SD, FD
SE2SC	Mf > I > CF, SD
SE3SC	Mf > Mm, Mc, SD

I : Isotropic, Mf: fine mosaics, Mm: Medium mosaics, Mc: coarse mosaics, SD: small domains, D: domains, FD: flow domains, CF: coarse flow textures

Table 6 Dilatation data of the blends of unprocessed and processed lignite samples (Group 1) with the coking coal CCl[a]

Sample code	Wt % in the blend	O_s (°C)	O_c (°C)	O_d (°C)	C	D
CC1	100	377	437	480	28	127
T	15	370	459	479	27	23
	25	390	458	-	13	-
TN1	15	347	423	472	28	88
	25	336	414	481	27	72
TN2	15	350	424	482	27	118
	25	335	414	478	24	91
TN3	15	350	429	480	27	92
	25	350	432	480	25	57
C	15	363	438	466	26	-15
	25	377	477	-	27	-
CN1	15	352	425	478	27	105
	25	330	420	480	27	70
CN2	15	347	415	473	26	130
	25	333	403	470	23	135
CN3	15	349	418	476	24	105
	25	353	427	469	20	64
S	15	369	442	480	24	32
	25	366	454	-	23	-
SN1	15	360	438	480	26	59
	25	351	436	483	23	28
SN2	15	368	438	480	24	67
	25	353	432	466	22	37
SN3	15	354	429	485	28	90
	25	338	421	473	26	85

[a]O_s softening temp. ; O_c:temp. at max. contraction; O_d :temp. at max. dilatation ; C: % max. concentration ; D: % max. dilatation

Table 7 Dilatation data of the blends of unprocessed and processed lignite samples (Group 2) with the coking coal CC2 and the tensile strength of the cokes obtained from the same blends[a]

Sample code	Wt % in the blend	O_s(°C)	O_c(°C)	O_d(°C)	C	D	TS (MN/m²)
CC2	100	384	443	488	25	108	4.12[b]
							4.80[c]
T	15	382	447	488	20	13	0.80
	25	379	449	-	15	-	0.10
TE1	15	358	431	478	26	78	5.36
	25	354	430	474	24	54	4.72
TE2	15	363	432	483	30	75	5.41
	25	357	434	480	24	50	4.86
TE3	15	374	446	479	24	63	4.60
	25	374	441	476	21	33	3.24
C	15	378	446	-	20	-	0.12
	25	379	450	-	19	-	0.00
CE1	15	358	433	485	28	76	5.10
	25	334	415	475	27	42	4.54
CE2	15	370	439	485	24	77	5.50
	25	356	432	481	24	57	4.76
CE3	15	372	438	481	25	65	4.46
	25	367	442	485	23	39	3.52
S	15	380	448	481	22	17	0.36
	25	370	448	-	20	-	0.00
SE1	15	372	442	481	23	58	2.96
	25	366	446	482	23	17	1.50
SE2	15	365	437	478	25	64	3.96
	25	365	437	485	22	47	3.02
SE3	15	364	432	476	25	65	3.54
	25	369	442	478	23	45	2.82

[a]same as in Table 6
[b]tensile strength of the coke produced in the industrial coke oven
[c]tensile strength of the coke produced in the laboratory coke oven

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Table 8 Operational parameters in circulating-gas mode of operations and results of polarized microscopic investigations (anisotropy) and the tensile - strength tests.

Code	F(L/min)	P_{op}(MPa)	T_{op} (^{0}C)	Anisotropy	TS(MN/m^2)
TF1	20±1	5.0±0.2	380±3	+	3.9±0.2
TF2	30±2	5.0±0.3	381±2	++	4.3±0.3
TF3	40±2	5.1±0.3	379±3	++	4.6±0.3
TP1	30±2	3.5±0.2	381±2	+	4.0±0.2
TP2	30±2	7.0±0.3	380±2	++	4.4±0.3
TP3	30±1	10.5±0.2	382±2	+++	4.9±0.2
TT1	30±1	5.0±0.3	350±2	+	3.8±0.2
TT2	30±2	5.0±0.3	381±2	++	4.3±0.3
TT3	30±1	5.1±0.2	400±3	++	4.4±0.2
CF1	20±1	5.0±0.2	381±3	+	3.8±0.2
CF2	30±2	5.2±0.3	380±2	++	4.2±0.3
CF3	40±1	4.9±0.2	379±2	++	4.4±0.3
CP1	30±2	3.5±0.2	380±1	+	3.7±0.2
CP2	30±1	7.0±0.2	381±2	++	4.5±0.3
CP3	30±1	10.5±0.3	380±2	+++	4.8±0.3
CT1	30±2	5.0±0.2	350±2	+	3.7±0.3
CT2	30±2	5.2±0.3	380±2	++	4.2±0.3
CT3	30±1	5.1±0.2	401±3	++	4.3±0.2
SF1	20±2	5.1±0.3	380±3	none	ND
SF2	30±2	5.2±0.3	381±3	none	ND
SF3	40±2	5.0±0.2	380±2	+	2.8±0.2
SP1	30±1	3.5±0.3	381±1	none	ND
SP2	30±1	7.1±0.2	382±2	none	ND
SP3	30±1	10.5±0.2	383±2	+	3.1±0.3
ST1	30±1	5.1±0.2	350±1	none	ND
ST2	30±2	5.2±0.3	381±3	none	ND
ST3	30±1	5.0±0.2	401±2	+	3.0±0.3

F: flow rate of coke-oven gas; no. of + signs shows the relative extent of anisotropy development; TS values belong to the cokes obtained from 25 % blend of treated lignite with the coking coal CC2 (refer Table 7). TF2=TT2; CF2=CT2 ; SF2=ST2

APPENDIX 2

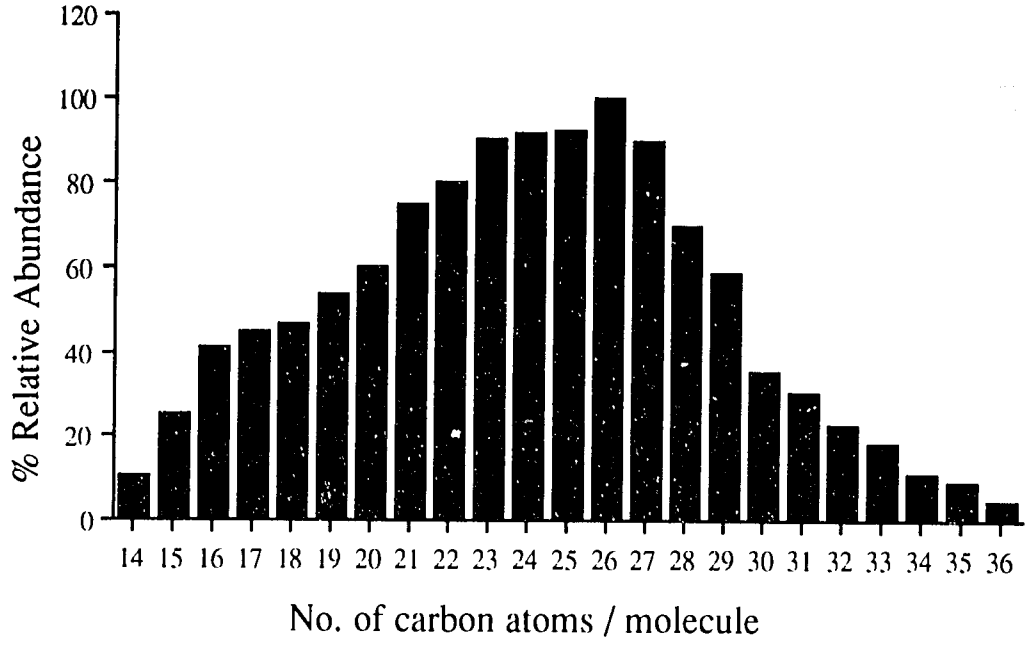

Figure 1 n- alkane composition of the n-hexane extract obtained from Çan lignite processed with coke - oven gas at 381^{0}C and 14.4 MPa operating conditions.

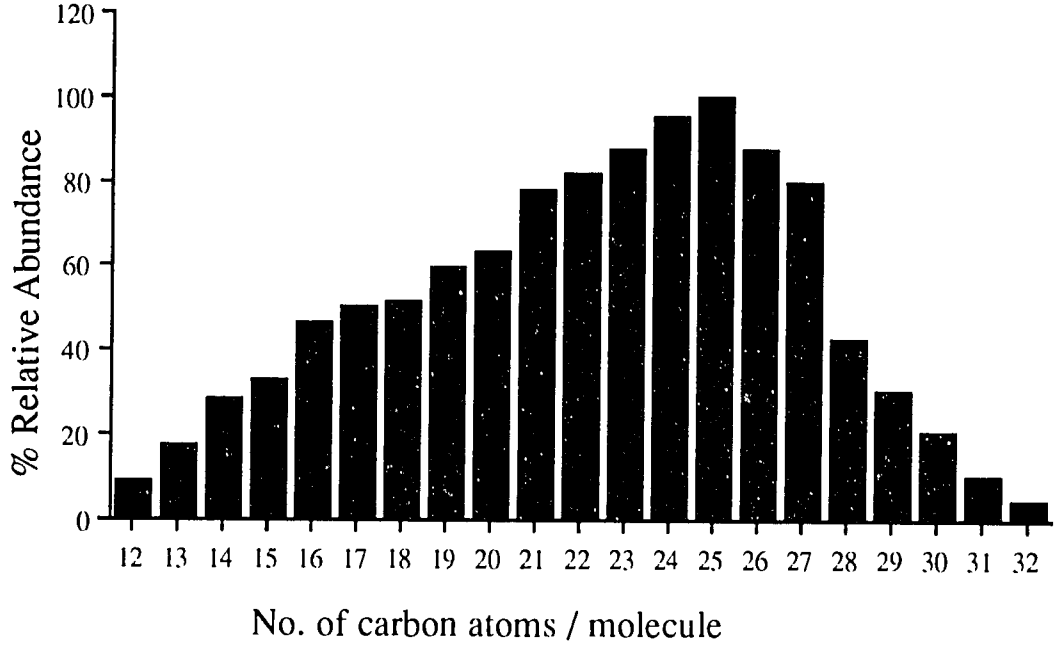

Figure 2 n- alkane composition of the n-hexane extract obtained from Soma lignite processed with coke - oven gas at 381^{0}C and 17.0MPa operating conditions.

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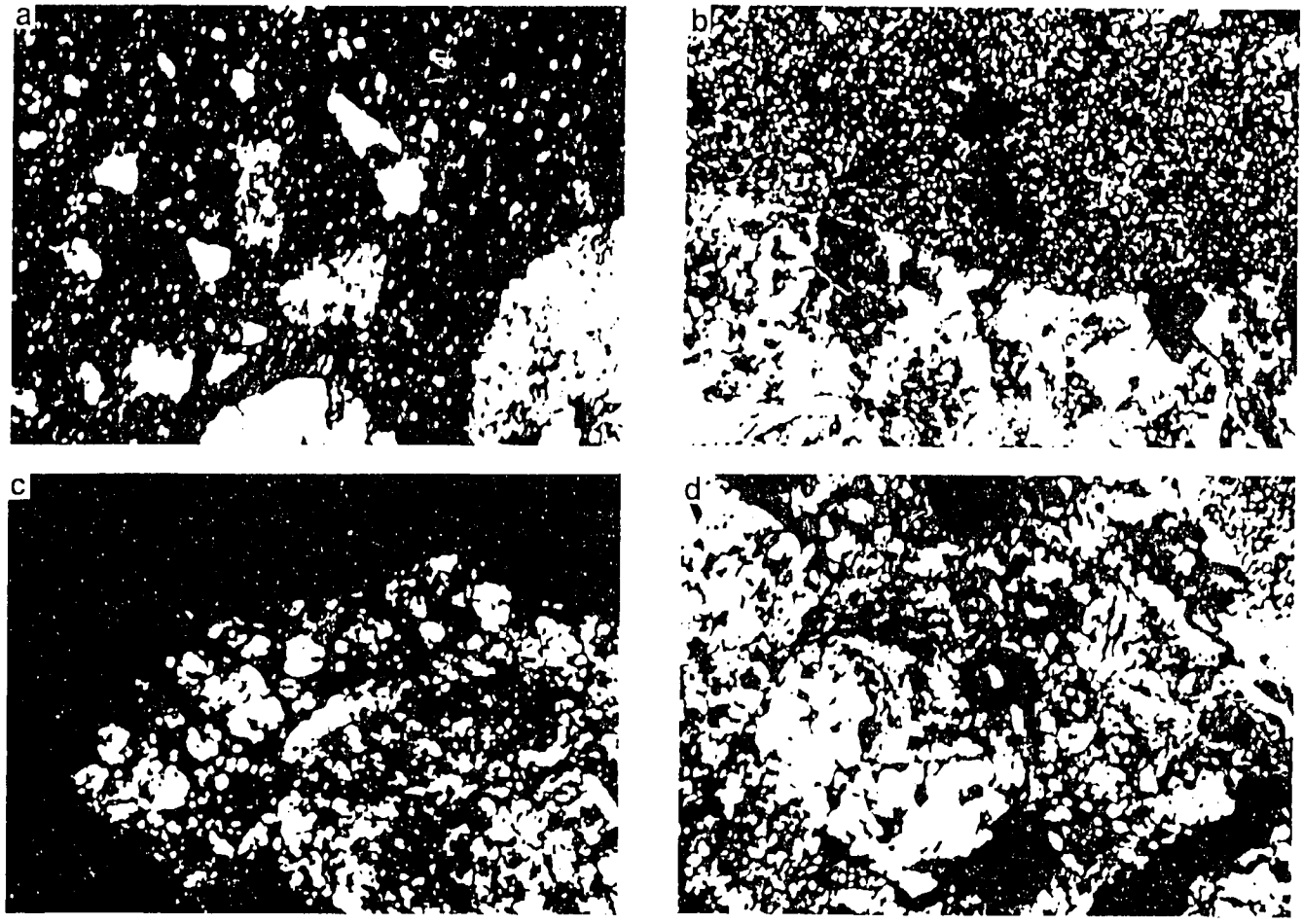

Figure 3 Optical micrographs of Tunçbilek lignite processed with coke-oven gas and of the corresponding semicokes obtained at 550 C. a. TF1, b. TF1SC, c. TF2, d. TF2SC

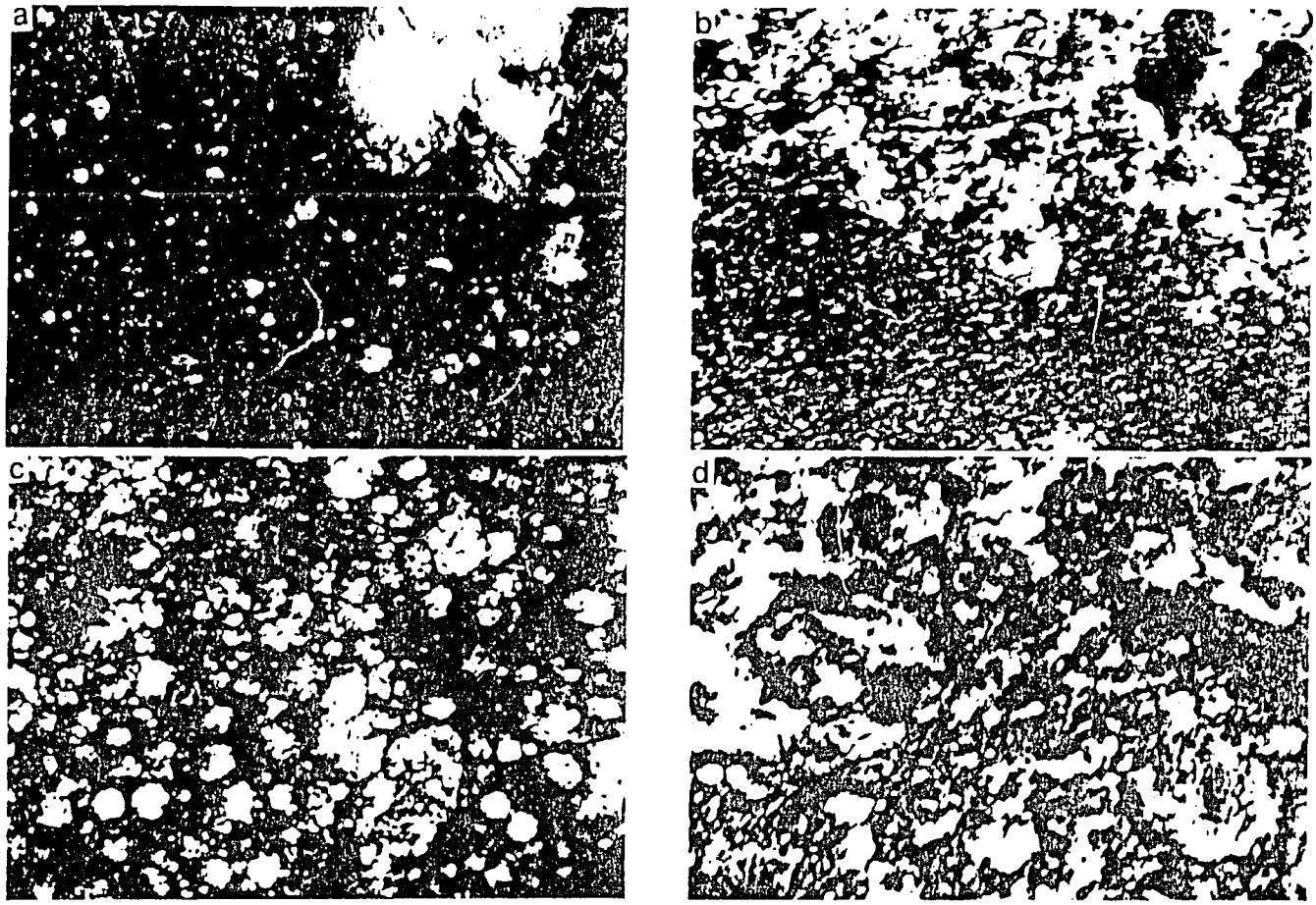

Figure 4 Optical micrographs of Çan lignite processed with coke-oven gas and of the corresponding semicokes obtained at 550 C a CE1 b. CE1SC, c. CE2, d. CE2SC

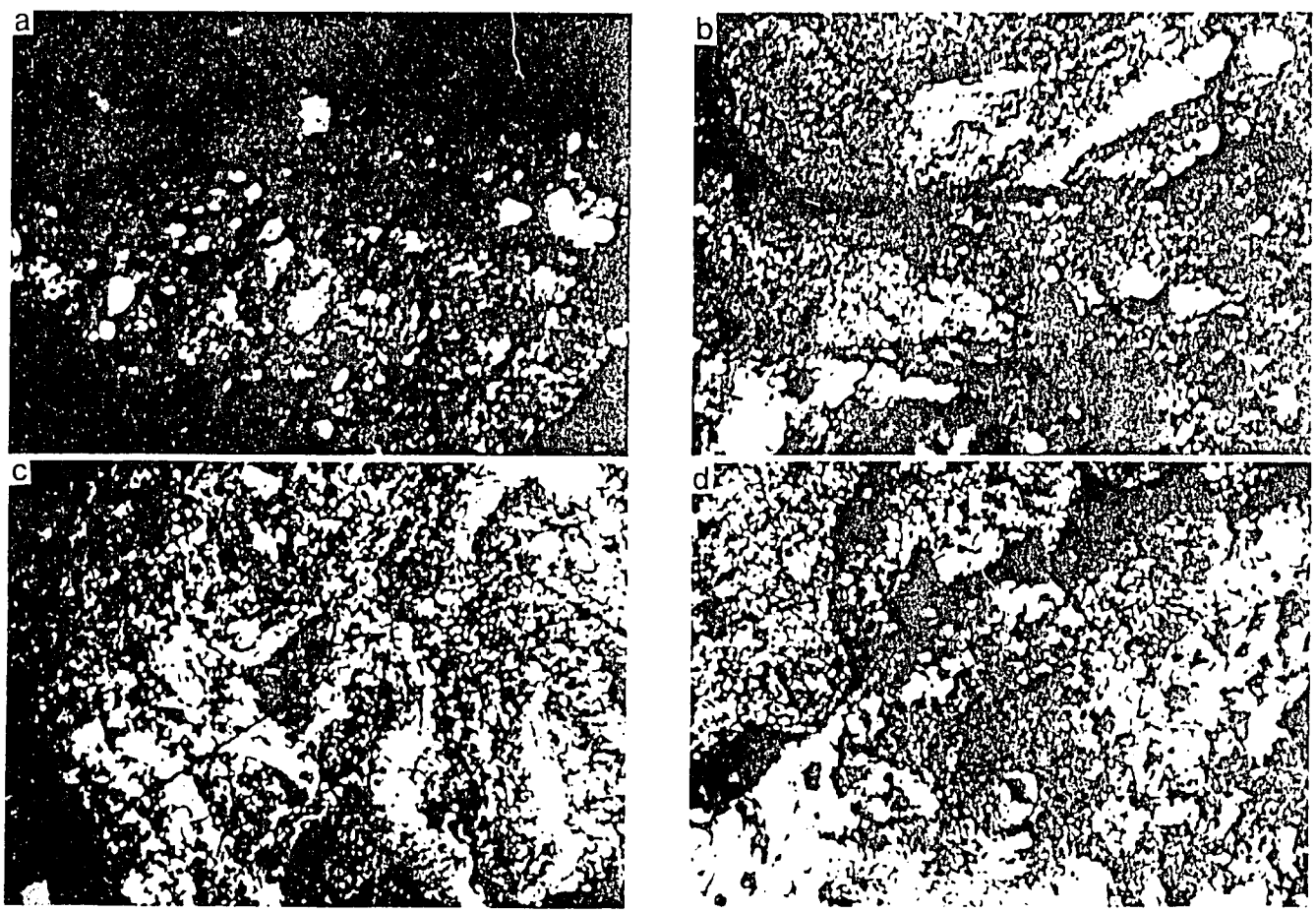

Figure 5 Optical micrographs of Soma lignite processed with coke-oven gas and of the corresponding semicokes obtained at 550 C a. SE1, b. SE1SC, c. SE2, d. SE2SC

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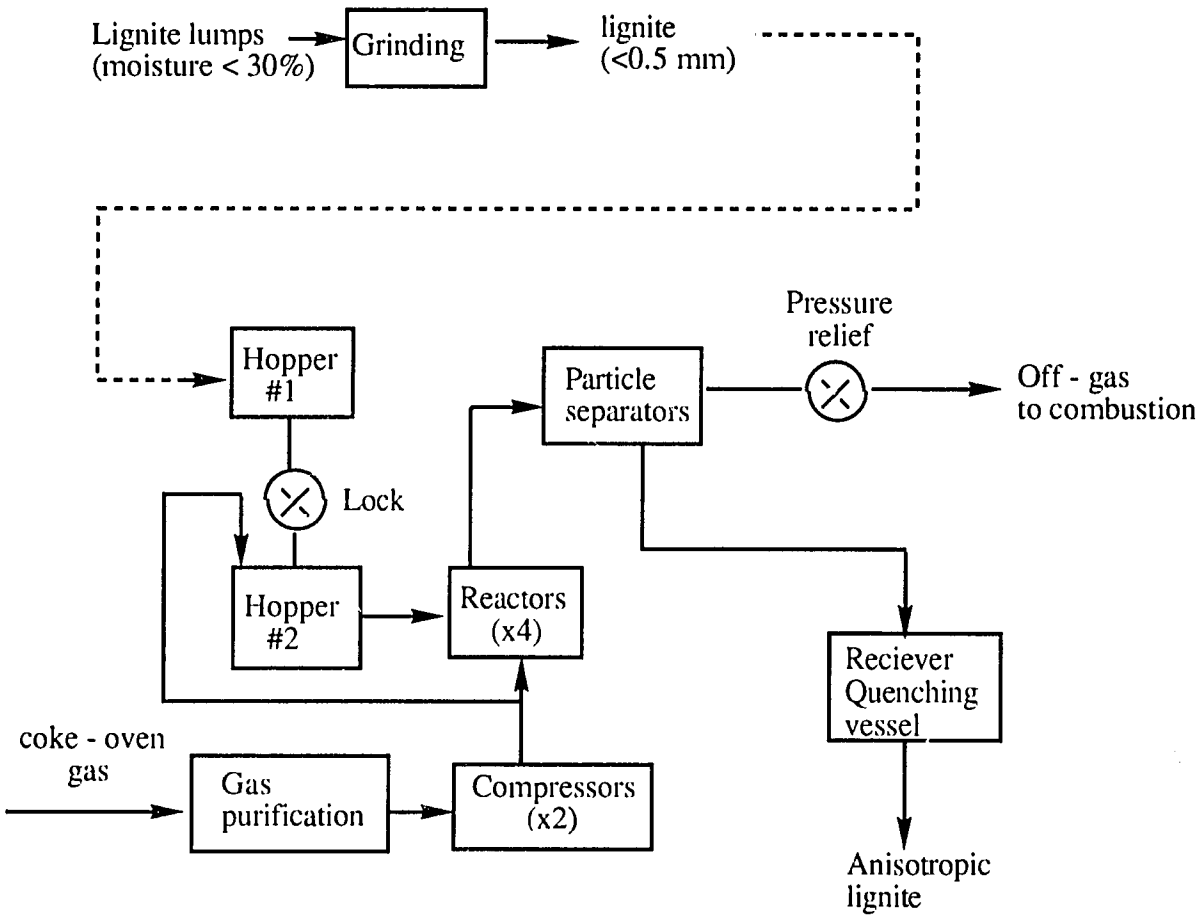

Figure 6. Schematic flow diagram of lignite processing with coke - oven gas.