

BOJANA D. ALEKSIĆ¹
BOGDAN R. ALEKSIĆ¹
BRANISLAV Ž. MARKOVIĆ¹
OLGA G. CVETKOVIĆ²
MARKO D. ERCEGOVAC³
DRAGOMIR K. VITOROVIĆ^{2*}

¹ IChTM – Center of Catalysis
and Chemical Engineering,
Belgrade

² IChTM – Center of Chemistry,
Belgrade

³ Faculty of Mining and Geology,
University of Belgrade

SCIENTIFIC PAPER

662.642:66.094.1(66.097)

DIRECT LIQUEFACTION OF SOFT BROWN COAL FROM THE KOSOVO BASIN

The behaviour of Kosovo Basin (Yugoslavia) soft brown coal was studied during a direct liquefaction process by catalytic hydrogenation. A stream of hydrogen was passed through a tetralin dispersion of the pulverized coal in the presence of commercial extruded hydrogenating-desulphurizing cobalt-molybdenum/alumina catalyst. The experiments were carried out in the temperature range between 365 and 440°C at 13.5 and 15.0 MPa, the reactants being kept at selected stationary working conditions for 1–8 hrs. The yields of liquid products soluble in *n*-heptane (light oils), asphaltenes (*n*-heptane insoluble liquid products) and the solid coal residue served as a basis for the estimation of coal reactivity and for the calculation of total coal conversion. The liquid product yields varied substantially depending on the reaction temperature and the residence time. The total conversion under most of the applied reaction conditions was found to be around 80%, the highest (~86%) being observed with the longest, 8 h residence time. Various types of grains of modified coal and newly formed types of coal grains, as well as mineral matter were identified by micropetrographic analysis, indicating the release of gases in the initial stages of hydrogenation and the formation of semi-coke and coke by the polymerization of liquid products in the later reaction stages.

The investigation of Kosovo Basin coal represents part of a research project involving the liquefaction of domestic soft brown coals, i.e. lignites, aimed at searching for ways for the more efficient utilization of low-rank coals, particularly those from the richest coal deposits in the country. Kosovo Basin coal has been used so far to a limited extent, primarily as an energy source in power plants. Therefore, it was of interest to study the potential of Kosovo Basin coal for obtaining various liquid products. A direct liquefaction process by catalytic hydrogenation, used previously in the liquefaction experiments of coals from Aleksinac [1], Kolubara [2–4] and Kostolac [5,6] basins, was also used for the liquefaction of Kosovo Basin coal. Due to differences in the petrographic compositions of different coals, the results observed for any individual coal could not be quite reliably used in determining the hydroliquefaction conditions for any other coal, even if they were of similar rank [7]. Hence, it is necessary to check the effect of individual process parameters on the nature and yields of the products of each individual coal sample [8,9]. The coal reactivity will depend not only on its chemical structure, but also on its physical properties [10], mineral matter content [11], the preparation procedure [12] and some other factors [13]. This paper describes the results of our study on the liquefaction behaviour of low-rank coal from the Kosovo Basin.

EXPERIMENTAL

Coal sample

The experiments were carried out with a sample of washed soft brown coal obtained from the Kosovo Mines, air-dried to equilibrium moisture and then crushed, ground and sieved.

The characteristics of the <160 µm coal fraction used in the liquefaction experiments are shown in Table 1.

Table 1. The characteristics of Kosovo Basin coal

Equilibrium moisture (wt %)	18.4
Ash (%)	16.6
Volatiles (wt %, dry basis)	40.7
Sulphur, total (wt%, dry basis)	2.0
Ultimate analysis (wt%, dry basis)	
Carbon	65.03
Hydrogen	5.13
Nitrogen	1.82
Oxygen + S _{org.} (by difference)	28.02
Heating value (kJkg ⁻¹)	
HHV	21686.1
LHV	20761.1
Macerals and minerals (vol. %)	
Huminite	69.0
Textinite	16.5
Ulminite	11.0
Atrinite	10.5
Densinite	20.0
Gellinite	6.5
Liptinite	7.0
Inertinite	2.5
Minerals	19.5
Clay	1.1
Pyrite	2.0
Carbonates	8.5
Gelification index	1.42
Huminite reflectance (% RR)	0.27 + 0.08
Xylite (wt%)	36.0

Liquefaction procedure

The liquefaction experiments analogous to those performed on other domestic coals [1–6] were carried out in a batch reactor with pulverized coal slurry in tetralin under a hydrogen stream and in the presence of

Author address: D. Vitorović, IChTM – Center of Chemistry, Studentski trg 16, 11000 Beograd, Yugoslavia;

E-mail: vitor@chem.ac.bg.yu

Paper received: March 5, 2000

Paper accepted: May 15, 2000

*Author to whom correspondence should be addressed;

e-mail: vitor@chem.ac.bg.yu; fax: +381 11 636 061

a commercial extruded hydrogenating–desulphurizing cobalt–molybdenum/alumina catalyst. The experiments were performed by direct catalytic hydrogenation under the pressures of 13.5 and 15.0 MPa in the temperature interval between 365 and 440°C and varying the reaction time from 1 to 8 hours. Details of the liquefaction procedure are described elsewhere [2,3].

Analysis of the liquefaction products

The yields of light oils (*n*-heptane soluble), asphaltenes (*n*-heptane insoluble) and the solid residue, as well as the composition of the liquid and gaseous products were determined by methods used in earlier coal liquefaction studies [3,14]. The coal conversion (*X*, %) was calculated on the basis of the dry, ash-free (daf) coal initial mass (m_c) and the dry ash-free (daf) solid residue (*R*), according to $X = 100(m_c - R)/m_c$.

The micropetrographic composition of the coal and the coal residue was analyzed according to ICCP standards [15].

RESULTS AND DISCUSSION

The yields of *n*-heptane soluble oil (*L_s*), asphaltenes (*L_A*) and the solid residue (*R*), observed at different temperatures and residence times, are shown in Figs. 1–3, respectively; the pressure was maintained at 13.5 MPa.

The effect of temperature was most pronounced on the yields of *n*-heptane soluble liquid products (*L_s*) (Fig. 1), except for 1h reaction time, when the increase of the yield was observed only at temperatures above 420°C.

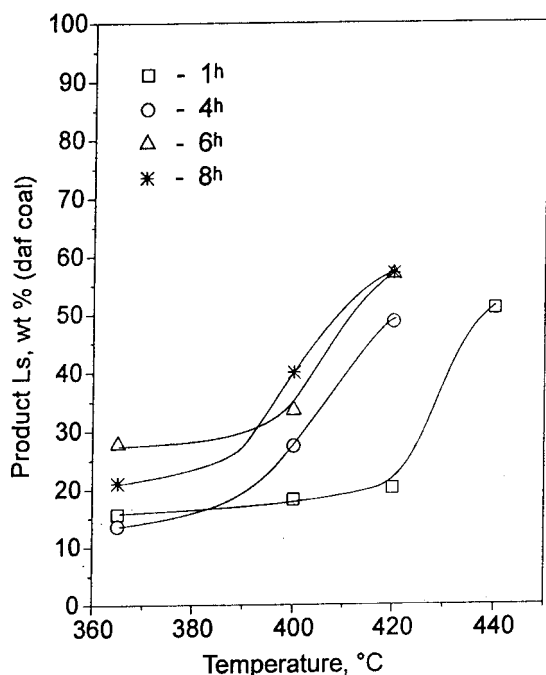


Figure 1. Yields of *n*-heptane soluble liquefaction products (*L_s*) at different temperatures and residence times.

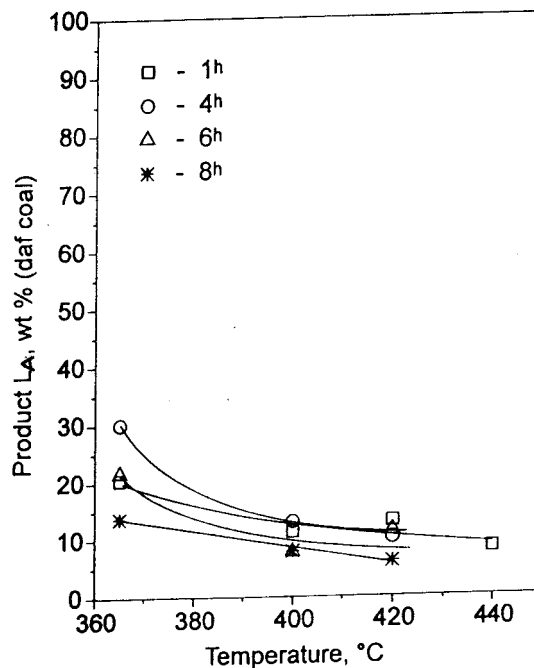


Figure 2. Yields of asphaltenes (*L_A*) at different temperatures and residence times.

However, at temperatures higher than 420°C it was not advisable to prolong the liquefaction experiments to 4, 6 or 8 hours, because the liquid products polymerized which made their separation by filtration impossible. Some difficulties in the filtration of the products were observed even in experiments at 420°C after longer residence times (6 and 8 h). This phenomenon was observed previously in the case of other soft brown coals [3], but only under the most severe conditions (440°C, 8 h, 16.5 MPa).

By prolonging the reaction time at constant temperature, the yields of light, *n*-heptane soluble oils

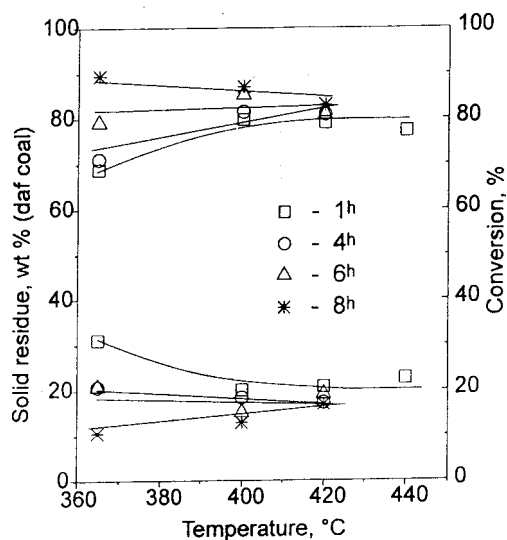


Figure 3. Yields of solid residue (*R*) at different temperatures and residence times and the corresponding coal conversion degrees (*X*).

(L_s), increased (Fig. 1), while the yields of asphaltenes (L_A) decreased (Fig. 2). The results of 1 h liquefaction tests differed to some extent. Namely, in the first stage of the process, the yields of light oils were lower and those of asphaltenes were somewhat higher, indicating that the heavy liquid products were not hydrogenated to greater extent during short reaction times, i.e., light oils were not yet produced on account of asphaltenes. According to the most commonly used interpretation of the direct catalytic coal liquefaction mechanism [16], in the first stages of the process, at the lowest temperature, coal dissolution generally begins in contact with the solvent, and the C–O, C–S, C–N and other bonds start to break by the simultaneous effect of heat and hydrogen in the presence of catalyst. The nature of the free radicals formed, which depends on the structure of the initial coal, will determine the extent to which they will be stabilized by hydrogenation or will unite into products of higher molecular mass, i.e., heavy oils, polymers or solid coke-type products [17].

Since the yields of both the light oils and asphaltenes during the first hour only changed slightly even at temperatures close to 440°C, the type of cross-linking in the structure of Kosovo coal might be supposed to be such as to permit the easy dissolution of one portion of the grains, the dissolution or disintegration of the remaining larger amount of coal substance requiring either substantially higher temperature or longer residence time at lower temperatures. Such behaviour in the liquefaction process was specific and was not observed in the case of other domestic soft brown coals investigated so far, suggesting a different structure and composition of Kosovo Basin coal.

The effect of pressure on the liquid product yields was slightly pronounced, as demonstrated by the example shown in Table 2.

Table 2. Liquefaction product yields and total coal conversion at different pressures ($t=365^{\circ}\text{C}$, $\tau=4\text{h}$)

p (MPa)	L _s , wt%	L _A , wt%	R, wt%	X (%)
13.5	13.3	30.1	23.0	76.9
15.0	13.9	30.7	20.8	79.2

Similarly to experience with other domestic soft brown coals [3,4], the effect of increasing the pressure above 13.5 MPa was much less important than the effect of temperature and residence time. Therefore, experiments at higher pressures were not discussed in more detail in this paper.

Changes in the composition of the gaseous products during the 4h experiments at constant pressure and temperature (13.5 MPa and 365°C) are shown in Fig. 4.

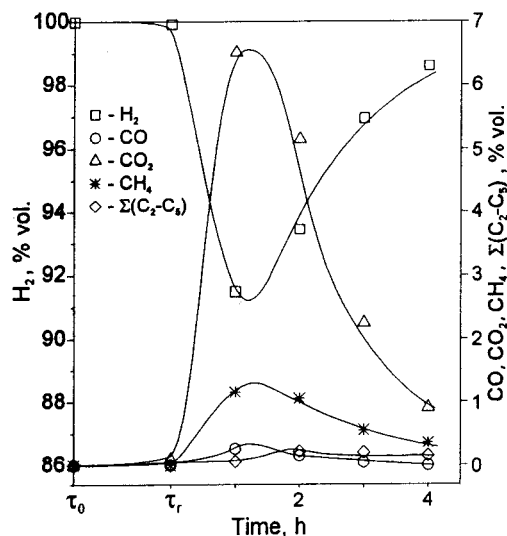


Figure 4. The composition of gases during 4 h liquefaction at 365°C and 13.5 MPa.

The most intense release of gases was observed during the first two hours upon reaching steady state reaction conditions. Subsequently, following a period of 4 h, the release of gases was practically neglectable. High amounts of gases in the initial stages led to high total coal conversions (Fig. 3) in spite of the relatively small simultaneous yields of liquid products (Figs. 1 and 2).

Changes in the composition of the gaseous products, depending on the reaction time in experiments at higher temperatures, are shown in Fig. 5 (a,b).

Similarly to liquefaction at lower temperatures, the gaseous product release was the most intense in the initial stages of the process. Gas chromatographic analyses of the gases obtained in 1 h experiments (Fig. 5a) carried out in 0.5 h intervals, indicated analogous changes in the concentrations of individual gases with time. Relative to liquefaction at a lower temperature (Fig. 4), a somewhat higher amount of gases was released at 420°C (Fig. 5b), resulting from the more intense thermal disintegration of coal at the higher temperature. The relatively high concentration of CO₂ was due to the higher proportion of carbonates in Kosovo Basin coal.

The following fifteen categories of grains were found by the micropetrographic analysis of the solid residues isolated after liquefaction: 1) unchanged (unreacted) coal; 2) changed (reacted) coal; 3) changed (reacted) coal (A-type); 4) humoplasts; 5) cenospheres (A,B); 6) grains of cross-linked structure; 7) semi-coke; 8) coke; 9) homogeneous high reflectance grains; 10) inertinite (fusinite); 11) fragments; 12) granular residue; 13) clay; 14) pyrite; and 15) carbonates. The changes in the composition of the solid residues were considered as a function of the reaction conditions, i.e., temperature and residence time. The most characteristic changes in the petrographic composition of the solid residues are shown in Table 3.

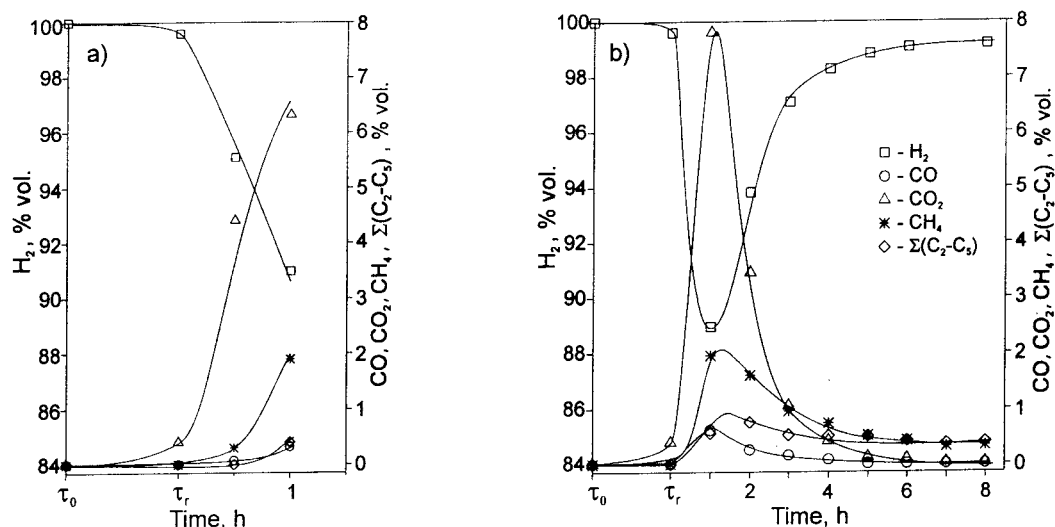


Figure 5. The composition of gases during 1 h (a) and 8 h (b) liquefaction at 420°C and 13.5 MPa.

Table 3. Petrographic composition of the solid residues

Categories of grains (vol %)	p = 13.5 MPa												
	t (°C)	365			400				420				440
	τ (h)	1	6	8	1	4	6	8	1	4	6	8	1
4 humoplasts		9.0	2.0	–	–	3.5	–	0.5	2.5	–	–	–	–
5 cenospheres													
A		9.5	1.0	0.5	–	3.5	5.5	1.5	3.5	1.0	1.5	3.0	2.0
B		3.0	1.5	–	–	–	1.5	0.5	0.5	–	–	–	–
7 semi-coke		2.5	6.0	3.0	2.5	5.0	3.0	2.0	9.5	8.0	8.0	6.0	10.0
8 coke		1.0	0.5	–	–	3.5	1.5	2.5	3.5	0.5	0.5	3.0	3.0
13 clay		10.0	36.0	63.5	19.5	17.0	34.0	23.0	25.0	30.5	22.5	21.0	15.0
14 pyrite		3.5	6.5	7.0	8.0	4.5	5.0	5.5	3.0	5.5	5.0	4.5	5.5

The appearance of humoplasts (cat. 4) under the mildest conditions (365°C, 1 h) is characteristic for the initial stages of coal structural changes. The proportion of humoplasts is subsequently reduced or they disappear at higher temperatures and longer reaction time. Humoplasts are followed by the formation of cenospheres (cat. 5) with one (A) or more vacuoles (B), which result from the elimination of certain parts of coal by dissolution or the release of gases, leading simultaneously to the formation of a cross-linked structure (cat. 6). The proportion of semi-coke (cat. 7) and coke (cat. 8) tends to be higher at higher temperatures, due to thermal processes and polymerization of the liquid products.

None of the solid residues contained unreacted coal (grain category 1), indicating that under all the applied conditions the coal did react with the solvent and/or hydrogen already at the beginning of the process. The grain categories 9–15 represent inert carboniferous and mineral components of the coal which remain in the solid residues. A high proportion of clay in the solid residues and a correspondingly low

total proportion of carboniferous components, indicate high coal conversion.

CONCLUSIONS

Direct liquefaction of Kosovo Basin coal by catalytic hydrogenation led to about 80% total conversion under the applied conditions. A maximum yield of *n*-heptane soluble light oils was obtained at 420°C in experiments which lasted 4, 6 or 8 h. In 1 h experiments the maximum yield required a temperature of 440°C. In liquefaction experiments at temperatures above 420°C and during longer reaction times, polymerization of the liquid products was observed, preventing separation of the products and, hence, determination of the yields. Relatively high conversions at low temperatures, even in the initial stages of the process, were due mainly to the release of gases and partly due to coal dissolution. This observation was confirmed by micropetrographic analysis which revealed grains containing carbonized membranes of the original coal macerals.

Acknowledgment

This work was supported in part by the Research Fund of Serbia (Project No. 0816). The authors are grateful to Kosovo Mines for providing the coal sample.

REFERENCES

- [1] M. Ercegovac, B.R. Aleksić, B.D. Aleksić, S. Bajc and D. Vitorović, in *Coal Science*, W. Peters Ed., Glückauf Verlag Essen, Düsseldorf, 1980, p. 573.
- [2] D. Vitorović, B.R. Aleksić, M.D. Ercegovac, B.D. Aleksić, S.I. Kontorović, B.Ž. Marković, O.G. Cvetković and S.M. Mitrovski, *Fuel* 73 (1994) 1757.
- [3] D. Vitorović, B.R. Aleksić, M.D. Ercegovac, B.Ž. Marković, O.G. Cvetković and B.D. Aleksić, *J. Serb. Chem. Soc.* 61 (1996) 129.
- [4] B.R. Aleksić, M.D. Ercegovac, O.G. Cvetković, B.Ž. Marković, T.L. Glumičić, B.D. Aleksić and D.K. Vitorović, in *European Coal Geology and Technology*, R. Gayer and J. Pešek, Eds., Spec. Pub. No. 125, 1997, p. 357.
- [5] B.R. Aleksić, M.D. Ercegovac, O.G. Cvetković, B.Ž. Marković, B.D. Aleksić, and D.K. Vitorović, *Fuel Proc. Techn.* 58 (1998) 33.
- [6] M. Ercegovac, B.R. Aleksić, O.G. Cvetković, B.Ž. Marković, B.D. Aleksić and D.K. Vitorović, *Ann. Geol. de la Penin. Balkanique, Belgrade LXII* (1998) 375.
- [7] R.E. Tischer and B.R. Utz, *Ind. Eng. Chem. Prod. Res. Dev.* 22 (1983) 229.
- [8] J. Černý, G. Šebor, J. Blažek and D. Maxa, *Erdöl, Kohle, Erdgas, Petrochem.* 48 (1995) 182.
- [9] M.D. Hetland, E.A. Sondreal, E.S. Olson and J.R. Rind, *Proc. 12th Ann. Int. Pittsburgh Coal Conf.* 1995, p. 1029.
- [10] F.J. Maldonado-Hóder, J. Rivera-Utrilla and A.M. Mastral-Lamarka, *Fuel* 74 (1995) 823.
- [11] J.T. Joseph and T.R. Forrai, *Fuel* 71 (1992) 75.
- [12] W. Böhlmann, R. Meusinger and W.D. Hoffmann, *Fuel* 73 (1994) 708.
- [13] R.M. Baldwin, in *Coal Science Symp. Ser. 641*, Amer. Chem. Soc., Washington, D.C. 1991, p.171.
- [14] D. Vitorović, B.R. Aleksić, S.I. Kontorović, B.D. Aleksić, M.D. Ercegovac, B.Ž. Marković, S.S. Bogdanov and O.G. Cvetković, *Fuel* 70 (1991) 849.
- [15] ICCP-Internationales Lexikon für Kohlenpetrologie, 2. Ausgabe, Paris, Centre National de la Recherche Scientifique, 1963, und Ergänzungen Band zur 2. Ausgabe, Paris, 1971.
- [16] J.H. Shinn, *Fuel* 63 (1984) 1187.
- [17] H.P. Stephens and R.J. Kottenstette, *Fuel* 70 (1991) 386.

IZVOD

LIKVEFAKCIJA MEKOG MRKOG UGLJA KOSOVSKE BASENE

(Naučni rad)

Bojana D. Aleksić¹, Bogdan R. Aleksić¹, Branislav Ž. Marković¹, Olga C. Cvetković², Marko D. Ercegovac³, Dragomir K. Vitorović²

¹IHTM – Centar za katalizu i hemijsko inženjerstvo, Njegoševa 12, 11000 Beograd

²IHTM – Centar za hemiju, Njegoševa 12, 11000 Beograd

³Rudarsko-geološki fakultet, Univerzitet u Beogradu, Djušina 7, 11000 Beograd

Ispitivano je ponašanje mekog mrkog uglja Kosovskog basena (Jugoslavija) pri direktnoj likvefakciji. Katalitička hidrogenizacija izvođena je u protočnom šaržnom reaktoru propuštanjem vodonika kroz suspenziju tetralina i usitnjelog uglja, u prisustvu komercijalnog presulfidiziranog Co-Mo/Al₂O₃ katalizatora. Eksperimenti su izvođeni na temperaturi 365 i 440 °C, pritisku 13,5 i 15,0 MPa, u trajanju 1–8 sati. Reaktivnost uglja je procenjavana i ukupna totalna konverzija izračunavana je na osnovu prinosa tečnih proizvoda rastvornih u *n*-heptanu (laka ulja), asfaltena (proizvodi nerastvorni u *n*-heptanu) i čvrstog ostatka. Konverzija uglja pri navedenim uslovima iznosila je oko 80 %, a najveća je bila (~86 %) pri najdužem reakcionom vremenu. Mikropetrografskom analizom identifikovane su različite vrste zrna modifikovanog uglja kao i novo stvoreni tipovi zrna uglja kao i mineralnog materijala. Dobijeni rezultati ukazuju da se gasovi oslobađaju u početnim fazama hidrogenizacije, a da polimerizacijom tečnih proizvoda polu-koks i koks postaju u kasnijim fazama hidrogenizacije.

Ključne reči: ugalj • meki mrki ugalj • Kosovski basen • katalitička hidrogenizacija • likvefakcija uglja •

Key words: Coal • Brown coal • Soft • Kosovo Basin coal • Catalytic hydrogenation • Coal liquefaction •