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Extraction of Brown Coals from Kansk-Achinsk and Lena Basins with Toluene and Water Containing Fluids

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The conversion of different brown coals from the Kansk-Achinsk and Lena Basins in an aqueous medium and in toluene containing mixtures with water and tetralin additives was studied under supercritical conditions over the temperature range of 375–550 °C and at pressures from 7 to 40 MPa. It was found that the liquefaction of brown coals in the medium of toluene solvent with small amount of hydrogen-donor tetralin co-solvent effectively occurred at low temperature 400 °C. On the other hand, coal methanation, hydrolysis, and oxidation reactions with the predominant generation of methane, carbon dioxide, and hydrogen prevailed in the water containing mediums. In a supercritical toluene at 440 °C, the addition of a small amount of water (15 %) stimulated destruction of coals with the predominant production of liquid products and moderate gas yields. The use of calcium oxide, sodium hydroxide and hematite as the catalysts increased the yields of liquid products.

Keywords: brown coals, toluene, tetralin, supercritical conditions.

Introduction

Because of instability on world oil market, the diversification of energy carriers is practically implemented in many countries with the involvement of various nontraditional types of organic raw materials, primarily, coal, whose reserves are much greater than oil and gas reserves. However, coal is difficult for processing. The organic matter of coal (OMC) has a macromolecular structure with molecular-size pores [1]. Because of this, chemical transformations can be limited by a transfer of solvent molecules within OMC.

Along with the development of traditional technologies for coal conversion, the processes based on the chemistry of extreme actions attract increasing attention. In particular, supercritical coal extraction pioneered by U.K. National Coal Board [2,3] provides a promising method to overcome some difficulties in the traditional coal liquefaction processes [3–14]. The supercritical solvents have

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an increased dissolving power, a low viscosity, and high diffusion coefficients, which are close to those of gases. This makes it possible to increase the conversion and selectivity of coal into liquid products which can be easily separated from the solid coal residue (mineral matter and unconverted organic matter) by depressurization.

Various organic substances (aliphatic and aromatic hydrocarbons, alcohols, and heterocyclic compounds) are used as solvents. Tetralin exhibits usually high efficiency due to hydrogen donor ability [10]. Toluene is of special interest to technology because it is a typical component of low-boiling fractions obtained in various coal conversion processes, and has easily attainable critical temperature (318,6 °C), pressure (4,11 MPa), and density (0,292 g/cm³) [4, 5, 11, 14–16]. However the degrees of coal conversion in toluene solvent are usually low [4, 17]. According to Kershaw et al. [4], the conversion of Australian brown coals varied from 30 to 35 % at 400 °C and was more lower for medium-rank coals even at a temperature of 425 °C [17]. Co-solvent additives are used to increase the solvent power and the efficiency of coal processing with toluene [4, 6, 8, 18]. According to [4], the conversion of brown coal in a supercritical toluene with the tetralin additive of only 5 % increased by 10–15 %.

Water is an unique solvent in terms of abundance and, environmental and technological safety ($T_c = 374$ °C, $P_c = 21,8$ MPa, and $\rho_c = 0,322$ g/cm³). It has been shown that water stimulates the cleavage of ester bonds [9, 19–22] and provides thus deep conversion of organic matter of coal. The efficiency of processes in the solvents under supercritical conditions can be improved also by using the appropriate catalysts [25, 26].

The objective of this paper was to study the conversion of brown coals from different deposits with supercritical toluene fluid with tetralin and water co-solvents and the effects of the catalysts on the conversion.

Experimental

The samples of brown coals from the Borodino deposit of the Kansk-Achinsk Basin and Kangalas and Zhigansk deposits of the largest Lena Basin were used in this study. The characteristics of the composition of coals are shown in Table 1 and 2. The data show that the coals differed with the composition of both organic matter and mineral constituents.

The solvent extraction of coals was performed in a rotating 250 ml autoclave. A 15-g portion of coal samples and required amounts of solvents were loaded in the autoclave. Toluene and the mixtures of toluene with water and tetralin additives were used as the solvents. Calcium oxide (3 wt % on an OMC basis), sodium hydroxide (2 wt %) and a fine powder of hematite (50 m²/g) served as the catalysts. The charged autoclave was purged with argon to remove air. The reaction was started by heating (10 K/min) the autoclave up to the required temperature in the range of 375 to 550 °C. The reaction time at a specified temperature was 1 h. The autogenous pressure in the autoclave during the reaction depending on the content of solvents attained 40 MPa.

After completion of the reaction and cooling of the autoclave, the volume and composition of the gases produced were measured, and solid and liquid products were removed from the autoclave to a filter. The solid residue on the filter was exhaustively extracted with toluene in a Soxhlet apparatus. The degree of coal conversion was evaluated from the change in the ash content after the reaction. The yield of liquid soluble products was calculated by difference between the overall coal conversion and the yield of gaseous products.

Table 1. Composition of brown coals

Basin	Deposit	A^d , wt. %	Ultimate analysis, % on a daf basis				
			C	H	N	S	O
Kansk-Achinsk	Borodino	4.9	71.9	4.8	1.0	0.4	21.9
Lena	Kangalas	8.0	71.1	5.6	1.0	0.5	21.8
The same “	Zhigansk	11.5	67.7	4.8		27.5	

Table 2. Concentrations of the main components of brown coal ashes

Coal	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O
Borodino	52.0	6.0	25.0	5.0	6.0	0.3	0.3
Kangalas	53.0	15.0	17.0	3.0	7.0	2.0	0.6

Results and Discussion

The yield of organic matter extracted from brown coal samples by boiling toluene in a Soxhlet apparatus did not exceed 1-2 wt %. The extract yield of 22 wt % from Borodino brown coal was produced with supercritical toluene (toluene vapour pressure of 0,31 g/cm³) at the temperature of 400 °C (symbol a in Figure).

The addition of tetralin with hydrogen donor activity allows the conversion of coal to be greatly increased. Shown in Figure are the data on Borodino brown coal extraction with the toluene-tetralin mixtures depending on the density of toluene vapour, the density of tetralin vapour being constant (0,07 g/cm³). One can see from Figure that the addition of tetralin to toluene containing media results in large increase in coal conversion (by 2 times) and yield of solubles. The increase in toluene vapour density from 0,144 (subcritical conditions) to 0,350 g/cm³ (supercritical conditions), and total pressure from 7,0 to 12,5 MPa hardly affects the conversion of Borodino brown coal, the yields of gases being no more than 8 %. This means the conversion to depend mainly on hydrogen donor activity of tetralin co-solvent irrespective of sub- or supercritical toluene states.

Tables 3 shows the data on the conversion of Borodino and Kangalas brown coals in the aqueous solvent at various temperatures. In the experiments with Borodino coal at a supercritical point (at 375 °C and at a water vapour density of 0,322 g/cm³), the conversion was only 10 %, the gas yield calculated on the weight of organic matter of coal being 15 wt. %, i.e. more than coal conversion. As the temperature increased to 410 °C the conversion increased to 24 %. The yield of gaseous products increased to 21,5 wt. %, the yield of solubles being only 2,5 %.

The reaction with Kangalas coal was performed at high temperature of 550 °C to stimulate coal conversion. Supercritical conditions were not attained at this temperature because of too high working pressure up to 29-40 MPa even at the 0,13–0,17 g/cm³ density of water vapor. Under these conditions, the conversion of Kangalas coal attained 51–52 %, a lot of gaseous products (47,8-53,1 %) was produced (methane and carbon dioxide predominately). One can see from Table 4 that methane was the main component (53,9-57,9 %) at high temperature and low water vapour, whereas carbon dioxide (78,5-

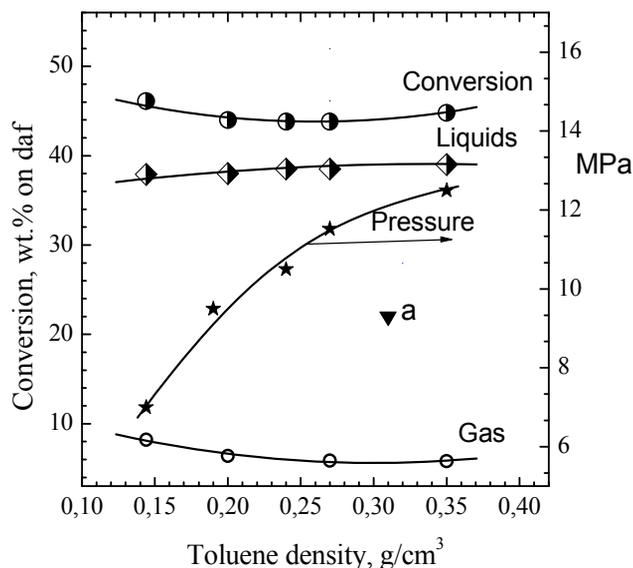


Fig. The conversion of Borodino brown coal in the toluene-tetralin mixtures depending on the toluene vapour density at 400 °C and constant tetralin vapour density of 0.07 g/cm³. The symbol a denotes the reaction in a single supercritical toluene

Table 3. Characteristics of brown coal conversion in the aqueous mediums

Deposit	Water vapor density, g/cm ³	Temperature, °C	Working pressure, MPa	Coal conversion, wt %	Yield, wt % on daf coal	
					gas*	solubles*
Borodino	0.322	375	22	10	15.0 (6.4)	- (3.6)
The same	0.380	410	35	24	21.5 (9.1)	2.5 (14.9)
Kangalas	0.130	550	29	52	47.8 (29.1)	4.2 (22.9)
The same	0.170	550	40	51	53.1 (30.9)	- (20.1)

*Shown in parentheses are the values recalculated based on a carbon balance in gaseous products.

Table 4. Composition of the gaseous products of brown coal conversion in the aqueous mediums

Deposit	Water vapor density, g/cm ³	Temperature, °C	Gaseous products, vol. %				
			CH ₄	CO	CO ₂	H ₂	other
Borodino	0.322	375	5.6	4.0	81.5	6.8	1.8
The same	0.380	410	13.4	2.9	78.5	5.0	0.2
Kangalas	0.130	550	57.9	0.8	23.0	16.5	1.8
The same	0.170	550	53.9	0.7	29.4	12.8	3.2

81,5 %) did at low reaction temperature and high water vapour. It appears from these data that the reaction of brown coals in aqueous medium at both low (375–410 °C) and high (550 °C) temperatures occurred mainly via gasification with moderate conversion into solubles.

Table 5. Brown coal conversion in the mixture of supercritical toluene with water additive at 440°C. Toluene and water vapor densities were 0.36 and 0.06 g/cm³, respectively

Deposit	Catalyst	Working pressure, MPa	Coal conversion, wt %	Yield, wt % on an OMC basis	
				gas	solubles
Borodino	–	32	31	14.7	16.3
The same	CaO	32	41	15.4	25.6
“	NaOH	33	39	19.1	19.9
Zhigansk	–	32	41	9.4	31.6
Kangalas	–	29	41	–	–
The same	CaO	34	51	14.9	36.1
“	NaOH	32	53	15.3	37.7
“	α -Fe ₂ O ₃	33	48	-	-

The data in Table 3 show that the yield of gases calculated on daf coal was close or even exceeds that of total coal conversion. This means that gaseous products resulted not only from the coal matter but also from water. Taking this into account, the recalculation based on carbon balance in gaseous products was made and percentage of carbon of coal converted into carbon containing gases (CH₄, CO₂ and CO) was evaluated, and then the percentage of carbon converted into solubles was determined. The recalculated data in Table 3 (in parentheses) show that the percentages of carbon of Kangalas coal converted into gases were 29-31 %, whereas the conversion into solubles increased to 20,1-22,9 % at 550 °C.

In the mixture of supercritical toluene with 15 % of water, the coals also underwent mainly gasification into CH₄ and CO₂ at the high temperature of 550 °C. At lower temperature of 440 °C dramatic decrease in the extent of gasification was observed. On the conversion of Borodino coal, the yield of gaseous products decreased to 14,7 % on daf coal. Unfortunately, it was impossible for the reaction in toluene mixture to recalculate the yield of soluble products based on carbon balance in the gaseous products. However, the yields of solubles determined by conventional procedure was not less than 31,6 % for Zhigansk coal and 16,3 for Borodino coal at 440 °C (Table 5).

The addition of catalysts allowed the conversion of coal at 440 °C to be increased by 7–12 % due to mainly soluble products (Table 5). In the presence of NaOH and CaO catalysts, Kangalas coal produced 36-38 % of soluble products, the yields of gases (primarily, CH₄ and CO₂), being no more than 15,3 % (Table 6).

Special autoclave experiments with toluene–water mixture were performed at 440 °C with no addition of coal to the autoclave. A little of gases was produced in the experiment without coal (by a factor of 20 as compared to that with coal). Mainly CO₂ (43,5 %) and H₂ (42,1 %) were present in the gaseous products, the concentration of CO was much less (14,4 %) and no methane was produced (Table 6). No products of toluene destruction (such as benzene) were also observed in the liquid phase. The data suggest that toluene was not subjected to demethylation with water under these reaction conditions, and toluene oxidation occurred to a very small extent. The production of gases in the presence of coal resulted thus from the reaction of coal oxidation and methanation with water.

Table 6. Composition of the gaseous products of brown coal conversion in the mixture of supercritical toluene with water additive at 4400C.

Deposit	Catalyst	Composition, vol. %				
		CH ₄	CO	CO ₂	H ₂	other
Borodino	–	33.1	9.0	47.4	6.5	4.0
The same	CaO	30.2	11.9	49.4	7.3	1.2
“	NaOH	34.1	0.4	55.5	8.4	1.6
Zhigansk	–	34.3	9.6	46.9	6.6	2.6
Kangalas	CaO	39.2	7.8	39.1	9.8	4.1
The same	NaOH	34.1	0.7	49.7	13.1	2.4
no coal	–	0.0	14.4	43.5	42.1	-

Data in Table 5 show that in terms of overall conversion and yield of soluble and gaseous products, Kangalas coal behaved more reactivity than Borodino coal. This can be due to less hydrogen content and to higher contents of alkali-earth metal compounds in Borodino coal. The latter has been shown [25, 26] to increase the density of cross-linking and to reduce the reactivity of organic matter for destruction.

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References

- [1] Krichko A.A., Gagarin S.G., Makar'ev S.S. // *Khim. Tverd. Topl. (Moscow)*. 1993. N 6. P. 27.
- [2] Bartle K.D., Martin T.G., Williams D.F. // *Fuel*. 1975. Vol. 54. N 4. P. 226.
- [3] Papic M.M., Whitehead J.C. // *CIM Bulletin*. 1985. N 11. P. 66.
- [4] Kershaw J.R., Overbeek J., Bagnell L.J. // *Fuel* 1985. Vol. 64. N 8. P 1070.
- [5] McHugh M.A., Krukonic V.J. *Supercritical Fluid Extraction: Principles and Practice*. Boston: Butterworth_Heinemann, 1994. 512 p.
- [6] Shishido M., Mashiko T., Arai K. // *Fuel* 1991. Vol. 70. N 4. P. 545.
- [7] Kolesnikova S.M., Kuznetsov P.N. // *Khim. Tverd. Topl. (Moscow)*. 2008. N 2. P. 21.
- [8] Sangon S., Ngamprasertsith S., Prasassarakich P. // *Proc. 12 Int. Conf. Coal Sci. Cairns, 2003*. P. 3B5 on CD ROM.
- [9] Townsend S.H., Klein M.T. // *Fuel*. 1985. Vol. 64. P. 635.
- [10] Kershaw J.R., Jezko J. // *Separation Sci. Technol.* 1982. Vol. 17. N 1. P 151.
- [11] Brunner G. *Gas Extraction: An Introduction to Fundamentals of Supercritical Fluids and the Application to Separation Processes*. Darmstadt: Springer, 1994. 387 p.
- [12] Rocha S.R.P., Oliveira J.V., Avila S.G. et al. // *Fuel*. 1997. Vol. 76. P. 93.
- [13] Yuan Q., Zhang Q., Hu H., Guo S. // *Fuel*. 1998. Vol. 77. P. 1237.
- [14] Murty Balijepalli S.N., Ravikumar Y.V.L., Dutt N.V.K. // *Fuel*. 1997. Vol. 76. N 2. P. 165.
- [15] Simsek E.H., Karaduman A., Caliskan S., Togrul T. // *Fuel*. 2002. Vol. 81. P. 503.

- [16] Hourcade M.L., Torrente C., Galan M.A. // Fuel. 2007. Vol. 86. P. 698.
[17] Philip Cahill P., Harrison G., Lawson G.J. // Fuel. 1989. Vol. 68. P. 1152.
[18] Kuznetsov P.N., Kolesnikova S.M., Kashirtsev V.A. et al. // Khim. Tverd. Topl. (Moscow) . 2010. N 4. P.14.
[19] Tanaka T., Tsutsumi A., Yoshida K., Inaba A. Abstracts of Papers Int. Conf. Coal Sci. Tokyo, 1989. P. 850.
[20] Townsend S.H., Klein M.T. // Fuel. 1985. Vol. 64. P. 635.
[21] Hu H., Go S., Hedden K.// Fuel Proc. Technol. 1998. Vol. 53. P. 269.
[22] Bermejo M.D., Cocero M.J., Fernandes-Polanco F. // Fuel. 2004. Vol. 83. P. 195.
[23] Barton P. // Ind. Eng. Chem. Process. Des. Dev. 1983. Vol. 22. P. 589.
[24] Sato Y., Chakrabarty S.K. // Liquid Fuels Technol. 1983. Vol. 22. P. 195.
[25] Kuznetsov P.N., Kuznetsova L.I. Khim. Tverd. Topl. (Moscow). 2008. N 6. P. 57.
[26] Kuznetsov P.N., Kuznetsova L.I., Bimer J. et al. // Fuel. 1997. Vol. 76. P. 189.

Экстракция бурых углей Канско-Ачинского и Ленского бассейнов в толуол- и водосодержащих средах

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Изучено превращение бурых углей Канско-Ачинского и Ленского бассейнов в водной среде и в смеси толуола с водой и тетралином при сверхкритических параметрах в температурном интервале 375-550 °С и давлении от 7 до 40 МПа. Установлено, что в среде толуола с добавкой небольшого количества соразвителя тетралина ожижение бурых углей эффективно происходит при низкой температуре 4000 °С. В водной среде проходят реакции метанирования, гидролиза и окисления бурых углей с образованием в основном газообразных продуктов (метана, диоксида углерода и водорода). В среде толуола в сверхкритических условиях при 400 °С добавление небольшого количества воды (15 %) стимулирует процесс деструкции углей с образованием преимущественно жидких продуктов при умеренном газообразовании. Применение в качестве катализаторов оксида кальция, гидроксида натрия и гематита позволяет увеличить выход жидких продуктов.

Ключевые слова: бурые угли, толуол, тетралин, сверхкритические условия.
