

Predicting the Possibility for Deep Hydroprocessing of Some Kuzbass Coals

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Abstract. Using thermal analysis and photoacoustic IR spectroscopy techniques, the abilities to be hydrogenated for some low-metamorphosed Kuzbass coals have been estimated in the aim of studying the possibilities of their deep industrial processing to obtain liquid fuels and valuable chemical products. Two independent parameters for quick assessment of solid fuel suitability for hydrogenation processes under high pressure of hydrogen have been proposed: 1) the relative maximal rate of coal pyrolysis in the 300-500°C temperature range, $[(1/m_0) \cdot dm/dT]$ (calculated from thermal analysis data), and 2) the intensity of aliphatic IR absorption bands (the sum of their optical densities), normalized to the optical density of an IR absorption band associated with aromatic ring C=C-bonds [i.e., $(D_{2920}+D_{2860})/D_{1600}$] (obtained from photoacoustic FTIR spectra of coal materials). It has been shown that for a number of low-metamorphosed Kuzbass coals (Barzas sapromixite, Itatsky lignite and Karakansky long-flame coal) the above mentioned parameters were in good consistency with generally accepted hydrogenation ability parameters of solid fossil fuels – atomic H/C ratios and volatile matter values.

1 Introduction

One of the most important directions for non-fuel use of coals is their hydrogenation processing to produce artificial liquid fuels and valuable chemical components. Processes of direct coal hydrogenation are usually conducted at the temperatures of 400-600°C under high hydrogen pressure (15-20÷70-80 MPa) [1-7]. For intensifying hydrogenation reactions and providing less severe conditions of coal conversion, these processes are often carried out in the presence of hydrogen-donor solvents (tetralin, alkyltetralins, phenanthrene and anthracene hydro-derivatives, high-temperature fractions of oil and coal-derived products) with using relatively inexpensive catalysts (compositions on the base of iron, molybdenum, tungsten, zinc, nickel and cobalt compounds or their mixtures) [2-7]. Analysis of literature data shows [2-5] that for effective occurring of hydrogenation processes, it is most expedient to use coals containing 65-85% of carbon, ≥5% of hydrogen (mass C/H ratio is not higher

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than 16-17), $\geq 30\%$ of volatile substances (on dry, ash-free basis), $\leq 5.5\%$ of ash content for hard coals and $\leq 10\%$ for brown coals (if ash content exceeds these values, then coal should be enriched), with fusened micro components content up to 15% and humidity up to 12%.

Among the coals that present within the Kuznetsk coal basin, the following low-metamorphosed solid fuels fully correspond to the above criteria: 1) Barzas sapromixites; 2) brown coals of the Itatsky deposit (lignites); and 3) long-flame and gas coals from the deposits of Belovo and Leninsk-Kuznetsk areas of Kuzbass, in particular, long-flame coals of the Karakansky-Western coal mine. In this paper, using the methods of thermal analysis and photoacoustic IR spectroscopy, an attempt has been made to estimate the possibility of using the Barzas sapromixite, Itatsky lignite and Karakansky long-flame coal as raw materials for direct hydrogenation processes under high hydrogen pressure.

2 Materials and methods

Proximate and ultimate analysis of coals was carried out using conventional methods (GOST standards). Derivatograms of coals in an inert medium were recorded with a Q1500D instrument (Hungary), which construction was modified by adding an ADC module I-7018P, produced by ICP DAS company (Taiwan), for analog-to-digital conversion of T, TG, DTA and DTG signals, followed by their registration on a personal computer using a SIMP Light program software (SIMP Light SCADA Company, Russia); the final mathematical processing of the data obtained was performed with an Origin Pro program complex (OriginLab Corp., USA). Sample charges in thermal analysis experiments were of ~ 200 - 220 mg; heating rate of $\sim 10^\circ\text{C}/\text{min}$; α -alumina precalcined at 1200°C was used as the reference standard; the pyrolytic experiments were conducted in a flow of helium (~ 450 He cm^3/min). Photoacoustic infrared Fourier transformed spectra (FTIR spectra) of the coals under investigation were registered with a Perkin Elmer 2000 FT-IR spectrometer (USA) equipped with a photoacoustic MTEC detector (Model 200); high purity electrode graphite was used as the reference standard.

3 Results and Discussion

Basic characteristics of three types of Kuzbass coals chosen (proximate and ultimate analysis data) are listed in Table 1. It is considered [2, 8] that the most reliable characteristics of coals hydrogenation abilities are their atomic H/C ratio and volatile matter (V^{daf}) values; reactivity in the process of hydrogenation increases with enhancing these parameters. However, as it was noted in [9], in a number of cases, an important characteristic of coal hydrogenation ability is the relative maximal rate of coal pyrolysis in the 300 - 500°C temperature range, i.e., the maximal rate of mass loss per 1 g of coal in an inert medium, $[(1/m_0) \cdot dm/dT]$, which value also correlates to the yield of liquid products in the process of coal hydrogenation. In order to evaluate this parameter in the present paper, we recorded the derivatograms of three types of low-metamorphosed Kuzbass coals in a flow of helium.

A typical view of such derivatograms (specifically, for Barzas sapromixite) is presented in Fig. 1. Three main temperature ranges of coal thermal decomposition are observed in these derivatograms: 1) 20 - 25 - 150 - 170°C (removal of adsorbed water), 2) 300 - 500°C (a primary or quick pyrolysis stage) and 3) >500 - 600°C (a secondary or slow pyrolysis stage). On the whole, the above described picture is characteristic for the processes of non-isothermal pyrolysis of solid fuels [10, 11]. In the primary pyrolysis stage, CO_2 , CO , H_2O , methane and its homologues, as well as light unsaturated hydrocarbons, are the prevailing components among the gaseous products released; these products are formed during the decomposition

of aliphatic structures and elimination of lateral substitutes from carbon-based framework of coal organic matter [10, 11].

Table 1 Characteristics of Kuzbass coals studied.

Coal sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%, <i>daf</i> basis)			H/C atomic ratio
	W ^a	A ^a	V ^{<i>daf</i>}	C	H	(O+N+S)	
Barzas sapromixite	3.4	40.5	66.2	84.1	9.5	6.4	1.36
Itatsky lignite	12.1	15.8	52.4	71.4	4.9	23.7	0.82
Karakansky long-flame coal	7.7	13.6	41.3	81.9	4.6	13.6	0.67

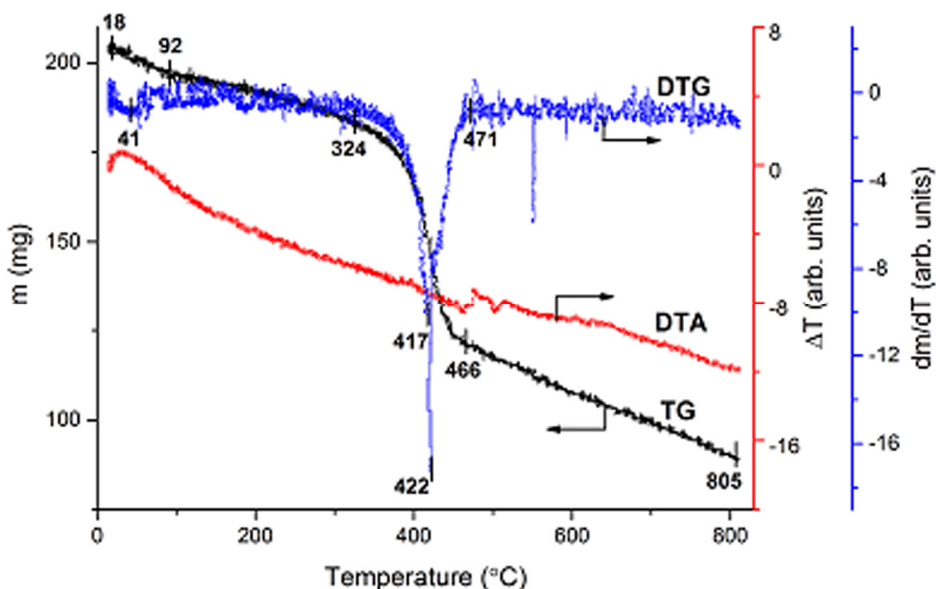


Fig. 1. A typical derivatogram of Barzas sapromixite in a flow of helium.

In the secondary (high temperature) pyrolysis stage, bond breaking and structural rearrangements of coal carbon-based matrix occur; in this process, the main gaseous products released are hydrogen and CO, as well as (in small quantities) CS₂ и HCN [11]. Calculated from derivatograms the relative maximal rates of pyrolysis in the 300-500°C temperature range for the Kuzbass coals studied, [(1/m₀) · dm/dT], are listed in Table 2. As it can be seen from these data, the values of these rates increase in the order of: Karakansky long-flame coal < Itatsky lignite < Barzas sapromixite.

To study the functional composition of coals under investigation, we used a method of photoacoustic IR spectroscopy. When recording IR spectra of solid and pasty materials, the main problem is that most of these samples are opaque in the IR spectral range and, therefore, are not available for measurement in transmitted light. As an alternative, various methods of analysis in reflected light are offered, but they also have their drawbacks. Thus, in order to register spectra of diffuse reflection, the sample often has to be strongly crushed (leading to destroy its crystalline structure), and, besides that, should be diluted using KBr; on the other hand, when using the method of disturbed total internal reflection (IRR), it is necessary to

take care of the reproducible optical contact with the surface of the sensor crystal [12, 13]. Photoacoustic spectroscopy (PAS) offers a simple and fast method of analysis for the majority of solid and powder samples. Since the photoacoustic effect produces a signal to be caused only by the energy absorbed by the sample, there are no here any undesirable obstacles, or they are very small. Therefore, the PAS method becomes more and more widespread when studying the structure of coals and carbonaceous materials [12, 14].

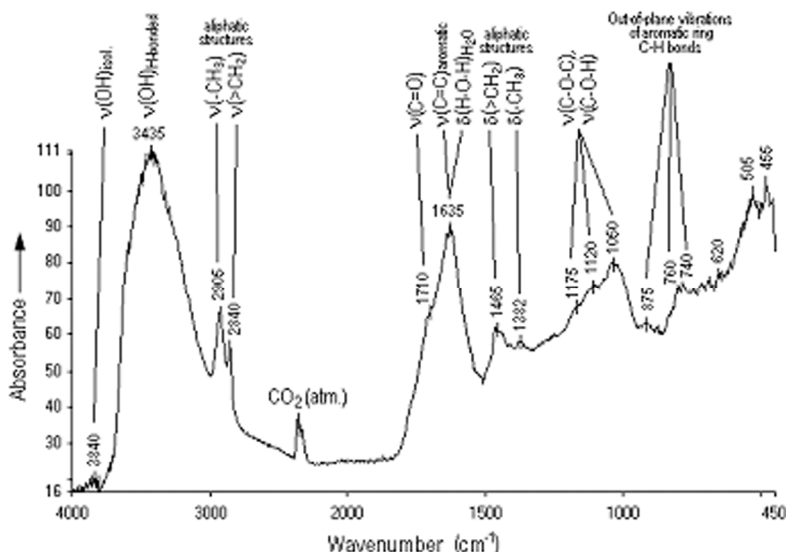


Fig. 2. A typical photoacoustic FTIR spectrum of Barzas sapromixite.

A typical photoacoustic FTIR spectrum of Barzas sapromixite is depicted in Fig. 2. Spectra of coals studied point out to the presence of broad IR absorption bands attributed to hydrogen-bonded OH groups ($3435\text{--}3485\text{ cm}^{-1}$), as well as weak signals related to isolated OH groups ($\sim 3840\text{ cm}^{-1}$); the spectrum of Barzas sapromixite is characterized by the increased (compared to spectra of Itatsky and Karakansky coals) intensity of IR absorption bands associated with aliphatic $\text{CH}_3\text{-}$ and $\text{CH}_2\text{-}$ groups (stretching vibrations at $2800\text{--}2900\text{ cm}^{-1}$ and deformation vibrations in the $1380\text{--}1460\text{ cm}^{-1}$ region) [2]. This is not surprising if we take into account the increased content of hydrogen in the elemental composition of the Barzas coal. The spectrum of this coal also clearly shows a shoulder with a maximum at 1710 cm^{-1} (stretching vibrations of carbonyl $\text{C}=\text{O}$ groups) against the background of the intense absorption band of aromatic ring $\text{C}=\text{C}$ bonds ($\sim 1600\text{--}1635\text{ cm}^{-1}$). It should be noted that this intense IR absorption band related to aromatic structures partly overlaps with a band of deformation vibrations of water at $\sim 1630\text{--}1650\text{ cm}^{-1}$. The presence of O-bridged C-O-C and C-O-H groups in the spectra under investigation is reflected by a group of IR absorption bands in the $1000\text{--}1200\text{ cm}^{-1}$ region. In the $700\text{--}900\text{ cm}^{-1}$ range out-of-plane vibrations of C-H bonds of aromatic rings are manifested [1, 2].

Table 2 Various hydrogenation ability parameters for the coals studied.

Coal sample	H/C atomic ratio	Volatile matter, V_{daf} (wt.%)	$[(1/m_o) \cdot \text{dm}/\text{dT}]^*$ $[(1/g_{\text{samp.}}) \cdot \text{mg}/^\circ\text{C}]$	$[(D_{2920}+D_{2860})/D_{1600}]^{**}$
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Barzas sapromixite	1.36	66.2	2.236	1.3447
Itatsky lignite	0.82	52.4	0.848	0.8125
Karakansky long-flame coal	0.67	41.3	0.742	0.7481

*Relative maximal rate of coal pyrolysis in the 300-500°C temperature range.

**A sum of optical densities of IR absorption bands related to aliphatic CH₂< and CH₃ groups, normalized to the optical density of an IR absorption band associated with aromatic ring C=C-bonds.

It is well known [1-3, 10, 11] that the solid fuel primary pyrolysis stage in the ~300-500°C temperature range corresponds to mainly thermal decomposition of aliphatic structures in coals. Since aliphatic structures can easily be identified in the IR spectra of coals (by IR absorption bands of CH₃- and CH₂< group stretching vibrations at 2840-2860 cm⁻¹ and 2900-2920 cm⁻¹, respectively [1, 3]), then the relative content of aliphatic structures in the coals studied (estimated from the data of their IR spectra) can serve as an additional independent parameter characterizing coal hydrogenation ability, along with the relative maximal rates of coal pyrolysis in the range 300-500°C and volatile matter values (*V^{daf}*) for them. In particular, a sum of optical densities of IR absorption bands attributed to C-H stretching vibrations in aliphatic structures (*D₂₉₂₀+D₂₈₆₀*), normalized to the optical density of an IR absorption band at ~1600-1630 cm⁻¹ associated with stretching vibrations of aromatic ring C=C-bonds (*D₁₆₀₀*), can be used as the above mentioned independent parameter for evaluation of aliphatic structure contents in solid fuels. The (*D₂₉₂₀+D₂₈₆₀*)/*D₁₆₀₀* values calculated from the photoacoustic FTIR spectra of coals studied are listed in Table 2.

In Figures 3 and 4, the proposed coal hydrogenation ability parameters, [(1/*m_o*) · dm/dT] and (*D₂₉₂₀+D₂₈₆₀*)/*D₁₆₀₀*, for the coals studied in the present work are compared to H/C atomic ratios and volatile matter values (*V^{daf}*) for the given materials. Analysis of these results shows that very good correlations (practically ideal linear dependences) are observed between the relative maximal rates of pyrolysis of low-metamorphosed Kuzbass coals in the 300-500°C temperature ranges, optical density ratios of aliphatic and aromatic IR absorption bands in these coals and H/C atomic ratios in the given materials (Fig. 3). Somewhat less satisfactory (but quite acceptable) linear dependences are observed between the proposed hydrogenation ability parameters and volatile matter values in the coals studied (Fig. 4). This means that the above described [(1/*m_o*) · dm/dT] and [(*D₂₉₂₀+D₂₈₆₀*)/*D₁₆₀₀*] parameters proposed for characterization of solid fuel reactivities, along with generally accepted parameters of coal hydrogenation ability (H/C atomic ratios and volatile matter values), can successfully be applied for an express assessment of the possibility of coal using as raw materials for hydrogenation processes under high hydrogen pressure.

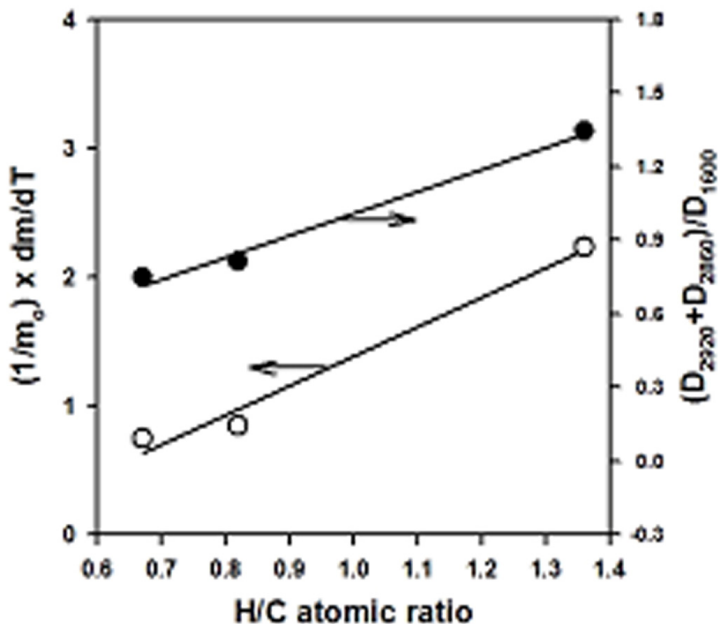


Fig. 3. Relationships between the H/C atomic ratios in Kuzbass coals, relative maximal rates of their pyrolysis in the 300-500°C temperature range (O) and $(D_{2920}+D_{2860})/D_{1600}$ optical density ratios of aliphatic and aromatic IR absorption bands (●) in these materials.

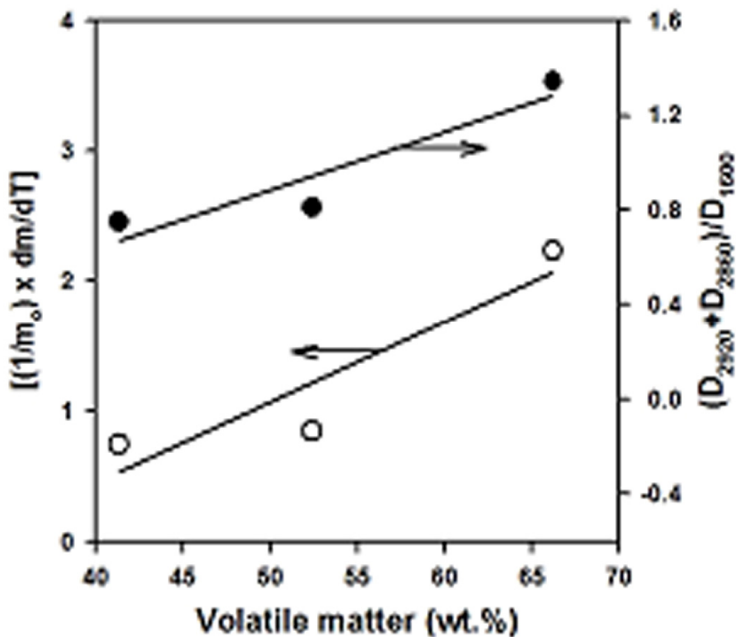


Fig. 4. Relationships between the volatile matter values in Kuzbass coals, relative maximal rates of their pyrolysis in the 300-500°C temperature range (O) and $(D_{2920}+D_{2860})/D_{1600}$ optical density ratios of aliphatic and aromatic IR absorption bands (●) in these materials.

4 Conclusions

The relative maximal rates of coal pyrolysis in the 300-500°C temperature range, $[(1/m_0) \cdot dm/dT]$ (calculated from thermal analysis data) and $(D_{2920}+D_{2860})/D_{1600}$ optical density ratios of aliphatic and aromatic IR absorption bands (obtained from photoacoustic FTIR spectra of coal materials) have been shown to be quite applicable parameters for preliminary express assessment of coals hydrogenation abilities (i.e., for checking possibility of using solid fuels as feedstocks in the processes of their direct hydrogenation under high hydrogen pressure).

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