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Research paper

IR spectra of low-metamorphosed Barzas coal thermally treated in hydrogen medium at various temperatures

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Abstract

The processes of coal breakdown into smaller fragments (radicals) taking place in hydrogen medium at high temperatures and pressures represent an important initial stage of the direct coal liquefaction (DCL) technology. In this work, with using a number of analytical techniques (FTIR spectroscopy, elemental, component and chromatographic analyses), the temperature effects (400-550°C) on the thermal transformations of low-metamorphosed Barzas coal (sapromixite) in hydrogen medium, have been investigated. Essentially similar extreme temperature dependencies of changes in the alkyl group relative IR intensities and the yields of “coal liquids” (maltenes and asphaltenes) have been established, with maximal values observed at T = 475°C. Also, a close relationship between the yields of gases and H/C atomic ratios for solid products of sapromixite conversions has been discovered.

Keywords: *Barzas coal; H/C atomic ratio; hydrogen medium; IR spectroscopy; thermal treatment*

1. Introduction

One of the possible ways to solve the problem of the world's liquid hydrocarbon resources depletion is to obtain liquid hydrocarbon products from relatively available and inexpensive solid fuels, e.g., from low-metamorphosed coals or wastes of coal-mining. At present, three main approaches are employed for converting solid fuels into liquid products: (i) coal pyrolysis; (ii) coal gasification with hydrogen-containing reagents for obtaining syngas [(CO + H_2) mixtures] and their subsequent hydroprocessing into hydrocarbons or oxygenates; (iii) direct coal liquefaction (DCL) in the presence of coal hydrogenation/hydrotreating catalysts [1]. The latter method is the most attractive since its theoretical efficiency can reach 70-75% [2-5]. DCL processes are usually carried out in the 400-600°C temperature range at rather high hydrogen pressure (15-20÷70-80 MPa) [3-7]. The resulting liquids are of much higher quality, compared with coal pyrolysis liquid products, and they can be used in chemical processes as a synthetic crude oil [3]. To intensify coal hydrogenation reactions and to provide its conversion under less severe conditions, the DCL processes are, as a rule, conducted in the medium of hydrogen-donor solvents with using relatively cheap and available catalysts (compositions on the base of Fe-, Mo-, W-, Zn-, Ni- and Co-containing compounds or their mixtures) [4-7]. According to the mechanism of DCL transformations [2, 4], this process begins with the initial destroying of coal matter into smaller fragments (radicals), which are then interacted with hydrogen to yield hydrogenated products or polymerize to form char. This is a mostly thermal decomposition process, in which the DCL catalysts do not have any marked participation. Taking into account an important role of this process in generating of coal liquids, the thermal treatment products of low-metamorphosed Barzas sapromixite (Kuznetsk coal basin, Russia), obtained in hydrogen medium (hydropyrolysis) at various temperatures, have been studied in this work using IR spectroscopic and some other analytical techniques.

2. Experimental

2.1. Barzas coal characteristics

The properties of Barzas coal studied are compiled in Table 1.

Table 1: Characteristics of as-received Barzas coal studied

Proximate analysis (wt.%)			Ultimate analysis (wt.%, *daf* basis)					H/C atomic ratio
W^a	A^a	V^{daf}	C	H	N	S	O (by diff.)	
4.2	22.2	64.0	82.74	8.83	0.54	1.22	7.33	1.28

Proximate analysis of Barzas coal was performed using well-known standard techniques [8], while ultimate analyses of this coal and solid products of its thermal treatment were carried out with a Flash 2000 instrument (Thermo Fisher Scientific, USA).

2.2. Thermal treatment of coal

A laboratory mini-autoclave (of ~ 20 cm^3 volume) was used to study thermal transformations of Barzas coal under examination. The autoclave with coal loaded was prepressured with hydrogen to various initial pressures at a room temperature and then heated at a rate of 10-12°C/min to the temperatures ranging from 400 to 550°C and to the final pressures attaining 7.0-11.0 MPa. The duration of heating at a certain temperature was of *ca*. 20 min, after which the autoclave was cooled by a fan to ambient temperature. Three kinds of the products formed in the course coal thermal treatment were obtaining after each experiment: 1) gaseous components; 2) resin-containing solid materials and 3) small amounts (3-5 wt.%) of liquid components representing aqueous solutions of organic compounds. The liquid phase components were observed only after the coal treatment at T = 475°C. The quantity of gases evolved after the autoclave cooling was controlled by a drum counter; all the solid and liquid products obtained after the reaction was finished were separating, weighing and directing to IR and chromatographic investigations, respectively. Besides that, the amounts of "coal liquids" (maltenes + asphaltenes) contained in solid phase products were measured by their sequential extraction with chemically pure *n*-hexane (to determine concentration of maltenes) and then analytically pure benzene (for separation of asphaltenes and non-extractable residues) in a Soxhlet apparatus. Preliminarily it was found that no maltenes and asphaltenes were present in the initial Barzas sapromixite samples. For each experiment on Barzas sapromixite thermal treatment in hydrogen, a material balance of solid, liquid and gas phase products formed was fixed. To ensure in reproducibility of the experimental results, each run was repeated, and the experimental deviations did not exceed more than 3%. Yields of coal conversion products were calculated as follows:

$$Y_g = [(m_c - m_s - m_w)/m_c] \times 100/(100 - A^a - W^a) \quad (1)$$

$$Y_w = [m_w/m_c] \times 100/(100 - A^a - W^a) \quad (2)$$

$$Y_m = [m_m/m_c] \times 100/(100 - A^a - W^a) \quad (3)$$

$$Y_a = [m_a/m_c] \times 100/(100 - A^a - W^a) \quad (4),$$

where Y_g, Y_w, Y_m and Y_a are the yields of gases, aqueous phase products, maltenes (soluble in *n*-hexane) and asphaltenes (soluble in benzene but insoluble in *n*-hexane), wt % [calculated on the dry ash-free (*daf*) basis], respectively; A^a and W^a are the ash and moisture contents in feed coal, wt %, respectively; m_c, m_w, m_s, m_m and m_a are the weights of feed coal, aqueous phase products, solid resin-containing products, maltenes and asphaltenes, g, respectively. The efficiency of coal liquefaction process (yield of "coal liquids") was calculated as a sum of the yields of maltenes and asphaltenes, wt % (*daf*).

2.3. Products characterization of thermally treated coal

A Fourier transform infrared (FTIR) spectroscopy technique was applied to determine the functional groups present in the solid products of Barzas coal thermal treatment; FTIR spectra of coal solid samples studied were registered using an Infralum FT-801 instrument (Lumex-Siberia, Russia) operating in the 500-4000 cm^{-1} range; a KBr disk pressing technique was used in these measurements. The spectra of extracted asphaltenes and maltenes were recorded in the form of thin films on KBr windows. Organic substances dissolved in the aqueous phase of Barzas coal conversion products were analyzed by a gas chromatography method using an Agilent 6890N system (Agilent Technologies, USA) equipped with a mass-selective Agilent 5973 detector. These analyses were conducted using a capillary column (HP-5ms) being heated in a programmable temperature regime; organic products to analyze were extracted from aqueous solutions with CH_2Cl_2.

3. Results and Discussion

3.1. FTIR spectra of Barzas coal

The results obtained are shown in Figs 1-8 and in Table 2. Typical FTIR spectra of as-received and thermally treated Barzas coals with the assignments of their main characteristic absorption bands (according to [9, 10]) are presented in Fig. 1. From these data it is obvious that the principal areas of IR absorption bands for sapromixite and the solid products of its thermal treatment are observed in the following spectral ranges: 3200-3700 cm^{-1} (stretching vibrations of OH groups); 3020-3080 cm^{-1} (stretching vibrations of aromatic C-H groups); 2920-2960 cm^{-1} (stretching vibrations of $>CH_2$ groups and asymmetric stretching vibrations of CH_3 groups); 2860-2880 cm^{-1} (symmetric stretching vibrations of CH_3 groups). Besides that, it should also be noted an intense peak at ~ 1600 cm^{-1} (stretching vibrations of aromatic C=C groups), which is partially overlapped with an IR absorption band ($\delta_{H\text{-}O\text{-}H}$) of H_2O deformation vibrations (~ 1630-1650 cm^{-1}). Other important IR absorption areas are: an absorption band centred at ~ 1700 cm^{-1} (stretching vibrations of C=O groups); absorption peaks in the 1430-1450 cm^{-1} region (bending vibrations of $>CH_2$ groups and asymmetric deformation vibrations of CH_3 groups) and at ~ 1380 cm^{-1} (symmetric deformation vibrations of CH_3 groups); an absorption peak in the 1100-1200 cm^{-1} region (stretching vibrations of C-O-H groups); a group of IR absorption lines in the 1020-1080 cm^{-1} interval with a maximum at ~ 1050 cm^{-1} (stretching vibrations of bridging ether C-O-C groups); several absorption bands in the 700-900 cm^{-1} range that are usually attributed to out-of-plane vibrations of C-H bonds in aromatic rings.

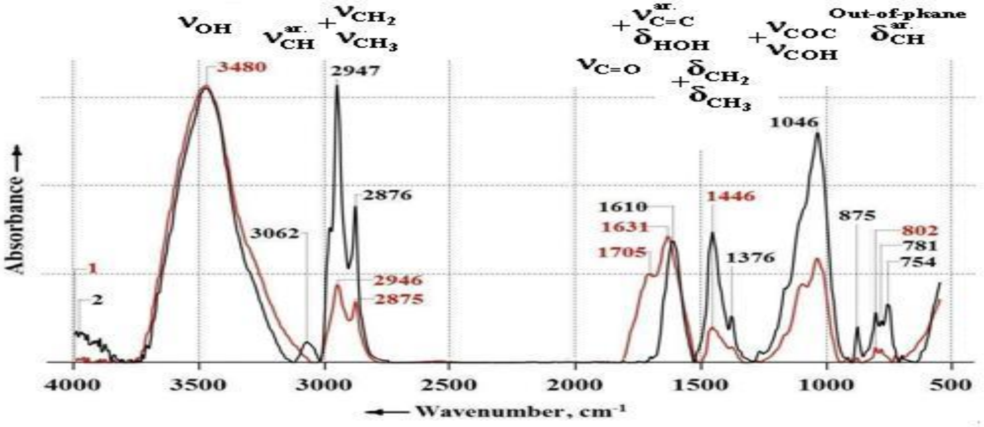

Fig. 1: Typical IR spectra of as-received and heat-treated Barzas coals: 1 – as-received coal; 2 – coal after thermal treatment at 475°C in H_2 for 20 min

3.2. Relationships between the IR absorption band intensities, yields of "coal liquids" and H/C atomic ratios in solid coal products

The relative intensities (optical densities) of alkyl groups expressed as the sum optical densities of CH_3 and CH_2 IR absorption bands normalized to the optical density of the 1600 cm^{-1} band, i.e., $(D_{2947} + D_{2876})/D_{1600}$ ratios, and the relative intensities of hydroxyl groups (D_{3480}/D_{1600} ratios), carbonyl groups (D_{1700}/D_{1600} ratios), C-

O-H groups (D_{1200}/D_{1600} ratios) and C-O-C groups (D_{1050}/D_{1600} ratios) were chosen as the basic parameters for quantitative assessment of thermal transformations in the Barzas coal samples after their thermal treatment in H_2 medium. The results of these quantitative estimations are shown in Figs. 2, 3.

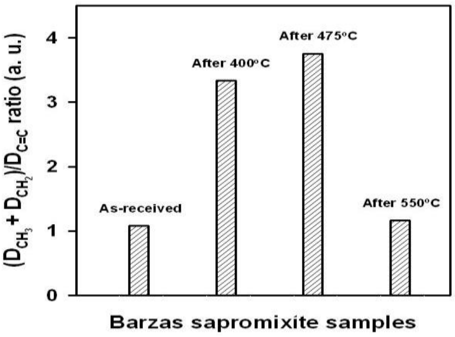

Fig. 2: Influence of temperature on the relative intensities of IR absorption bands related to alkyl groups in the FTIR spectra of Barzas coal samples thermally treated in H_2 medium

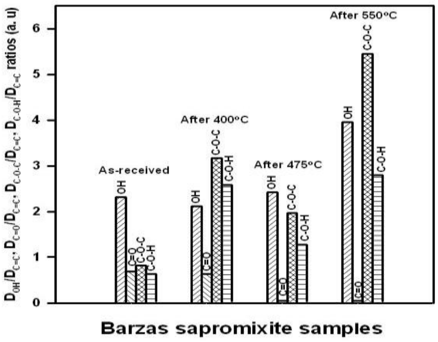

Fig. 3: Influence of temperature on the relative intensities of the IR absorption bands related to some O-containing groups in the FTIR spectra of Barzas coal samples thermally treated in H_2 medium

Data obtained points to a marked increase in alkyl groups absorption intensities with increasing the process temperature to 475°C (Fig. 2), which can be ascribed to the intense formation of paraffinic-naphthenic structures appearing during the coal heat treatment. However, at higher thermal treatment temperatures, the relative concentration of these groups decreases (Fig. 2), and this can be explained by an initial accumulation of alkyl-containing structures derived from the coal matter and their subsequent detachment from carbon matrix, followed by their transition into the gas phase.

Actually, at T = 550°C the yield of gases sharply increases, while the content of "coal liquids" (maltenes + asphaltenes) and H/C atomic ratio in the solid product significantly decrease (see Figs. 4 and 5). In fact, clear antibate dependence takes place between the gas yields and H/C atomic ratios in solid products of Barzas coal conversion (Fig. 5).

At the same time, both the yields of "coal liquids" (Fig. 4) and IR intensities of alkyl groups (Fig. 2) go through a maximum at 475°C with temperature rising. Thus, the optimal temperature for non-catalytic hydroconversion of Barzas coal into liquid products is about 475°C.

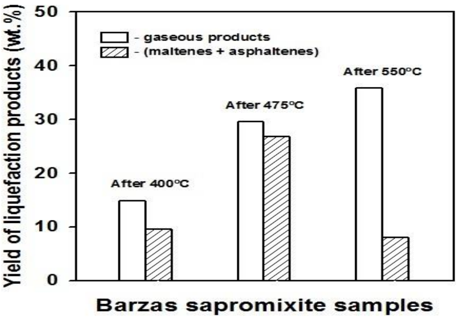

Fig. 4: Influence of temperature on the yields of liquefaction products (maltenes + asphaltenes) formed during the thermal treatment of Barzas sapromixite samples in H_2 atmosphere

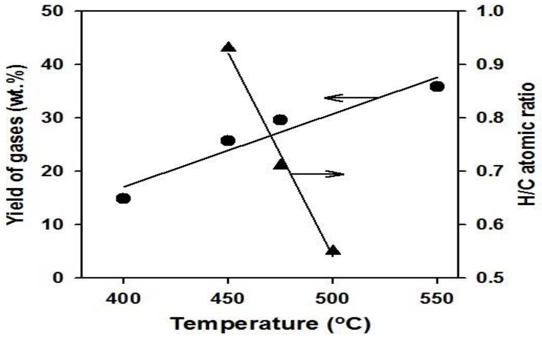

Fig. 5: Influence of temperature on the gas yields and H/C atomic ratios in the solid products of Barzas coal samples thermally treated in hydrogen atmosphere

Hydrogen medium is known to improve conversion of coal into liquid products, as compared to the similar experiments on coal decomposition in an inert atmosphere [11-13]. In other words, H_2 participates in coal transformations even when the reaction occurs in the absence of solvent or catalyst.

Vernon [14] proposed that the key role of molecular H_2 was to interact with free radicals of thermally treated coal directly for preventing coal radical sites from recombining with each other. Also, it has been assumed that the atomic hydrogen formed in the course of hydropyrolysis may additionally take a part in the destroying of some C−C bonds involved in forming the structure of coal matter [14].

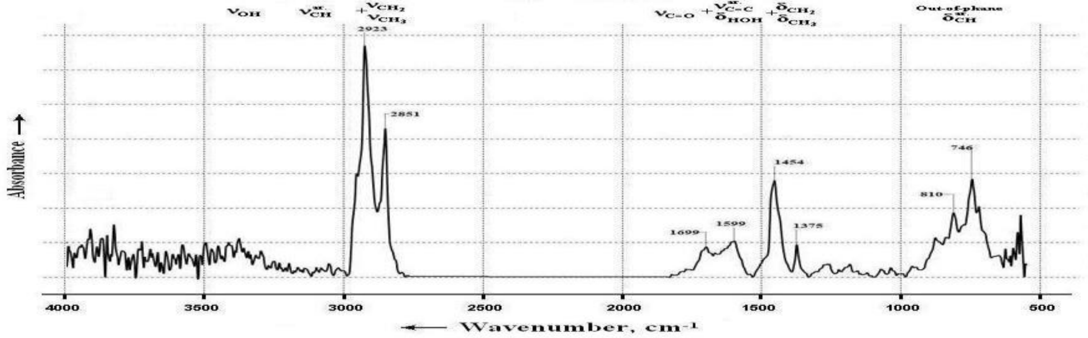

Fig. 6: A typical FTIR spectrum of maltenes extracted from solid products of Barzas sapromixite thermally treated in hydrogen medium (T = 475°C; P = 7.1 MPa; T = 20 min)

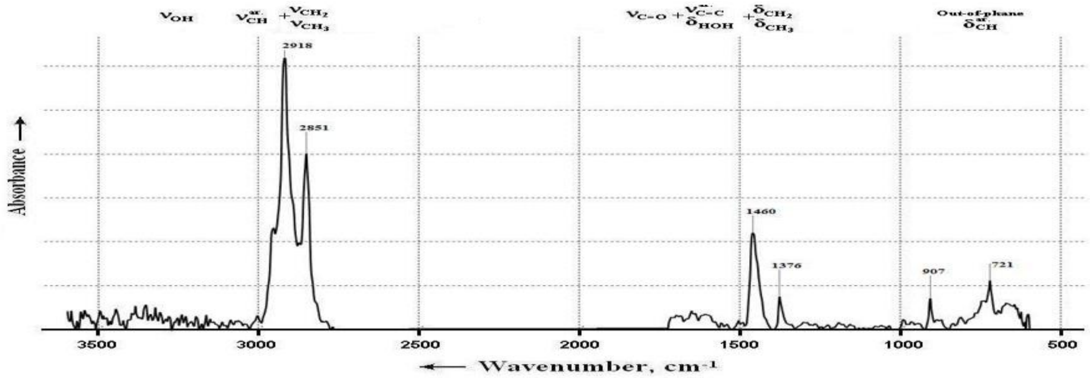

Fig. 7: A typical FTIR spectrum of asphaltenes extracted from solid products of Barzas sapromixite thermally treated in hydrogen medium (T = 475°C; P = 7.1 MPa; T = 20 min)

Since coal transformations studied in this work took place in a closed system (autoclave), the decrease in the yields of “coal liquids” at 550°C relative to 475°C may be explained by emerging secondary, retrogressive reactions of liberated volatiles recombining with the coal and/or by further converting of these volatiles into lower molecular gaseous products. Similar dependences were earlier observed by other researchers [8].

Changes in the IR absorption bands relative intensities for O-containing functional groups in the solid products of thermal reactions of Barzas coal (Fig. 3) points to the complex nature of its thermal transformations in H_2 atmosphere. Complicated dependences for variations in the IR intensities of O-containing groups may be caused by partial transition of oxygen atoms from C=O and O-H groups to the bridged C-O-C and C-O-H structures.

3.3. FTIR spectra of maltenes and asphaltenes, extracted from thermally treated Barzas coal

Functional compositions of "coal liquids“, i.e., maltenes and asphaltenes (their typical FTIR spectra are shown in Figs. 6 and 7, respectively), formed during heat treatment of the Barzas sapromixite, sharply differ from the functional composition of the initial coal (Fig. 1). The spectra of “coal liquids” contain predominantly paraffinic-naphthenic structures ($-CH_3$ and $>CH_2$ groups) and are characterized by practically absence of oxygen-containing functional groups. With increasing heat treatment temperature, the relative intensities of alkyl groups in maltenes tended to decrease, but in asphaltenes they increased (Fig. 8).

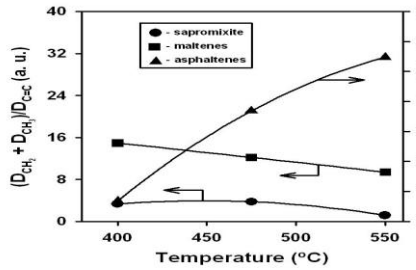

Fig. 8: Effects of thermal treatment temperature on the relative intensities of CH_2 and CH_3 groups in the FTIR spectra of Barzas coal and extracted from it maltenes and asphaltenes

This may be due to both the transfer of hydrogen from maltenes to asphaltenes, and the more rapid transition of hydrogen-containing structures (alkyl groups) from maltenes into the gas phase as the process temperature rises. It should be noted that when coal is converted in the presence of a hydrogen donor solvent, the solvent contributes more own hydrogen to coal hydrogenation and is more effective on the conversion of coal to oil, compared with gaseous H_2 [15]. From this standpoint, the maltenes formed in the given process may be considered as a hydrogen donor solvent for hydrogenation of asphaltenes in the coal under investigation.

3.4. Chromatographic analysis of organic components in the aqueous phase products

According to the chromatographic analysis results, among the organic substances identified in the aqueous phase of Barzas sapromixite conversion products prevailed various O-containing compounds, with phenol and its methyl- and dimethyl derivatives (cresols and xylenols) as the most valuable components (see Table 2). The relative total content of these mononuclear phenols in CH_2Cl_2 extract was of > 84.5%, with phenol concentration exceeding 39%.

Additionally, linear and cyclic ketones (pentanone, cyclopentanone, cyclohexanone, and other related compounds), as well as pyridine and low molecular weight organic acids (propanoic acid with its methyl derivatives, butanoic and pentanoic acids), have been discovered in the composition of organics present in the aqueous phase of Barzas sapromixite conversion products.

Relatively high contents of valuable monoaromatic phenols in aqueous phase products of Barzas coal conversion, in addition to highly hydrogenated resin-like maltene and asphaltene components present in coal solid products, makes the process of Barzas sapromixite hydrogenation rather attractive from the industrial point of view.

Table 2: Contents of organic compounds in aqueous phase products formed after Barzas coal thermal treatment (T = 475°C, H_2 medium)

Retention time (min)	Component	Relative concentration (wt. %)
2.035	Propanoic acid	1.862
2.089	2-Pentanone	1.057
2.132	Not identified	1.112
2.388	Not identified	0.514
2.492	Pyridine	0.698
2.632	Cyclobutene, 2-propenylidene-	3.661
2.839	Cyclopentanone	1.339
3.138	Pyridine, 2-methyl-	0.996
3.839	Pentanoic acid	1.170
4.040	Pyridine, 2,6-dimethyl-	0.656
5.009	Pyridine, 2,5-dimethyl-	0.468
5.795	Phenol	39.385
7.545	Phenol, 2-methyl-	16.099
8.069	p-Cresol	19.072
8.934	Phenol, 2,5-dimethyl-	1.058
9.739	Phenol, 2-ethyl-	1.361
10.007	Phenol, 2,4-dimethyl-	3.988
10.507	Phenol, 4-ethyl-	0.823
10.568	Phenol, 3-ethyl-	1.731
10.812	Phenol, 2,6-dimethyl-	0.595
11.238	Phenol, 3,4-dimethyl-	0.407
14.944	1,3-Benzenediol, 2-methyl-	0.478
16.231	1,4-Benzenediol, 2,5-dimethyl-	1.006

In future we are planning carrying out the experiments on Barzas sapromixite conversion in the presence of various catalysts and hydrogen donor solvents.

4. Conclusion

1. Using a number of analytical techniques (FTIR spectroscopy, elemental, component and chromatographic analyses), the influence of temperature (400-550°C) on the thermal behavior of low-metamorphosed Barzas coal (sapromixite) treated in hydrogen medium has been investigated.
2. With temperature increasing, the yields of "coal liquids" (maltenes + asphaltenes), as well as the relative IR intensities of alkyl groups ($-CH_3$ and $>CH_2$) in the solid products of Barzas coal, first increase, then go through a maximum at ~ 475°C and, at last, tend to decrease at higher temperatures of coal thermal treatment. This can be explained by the initial accumulation of alkyl-containing structures and their subsequent transition into the gas phase.
3. It has been established that H/C atomic ratios in the solid products of thermally treated Barzas coal tended to decrease while the yields of gases formed during its hydropyrolysis, vice versa, increased.
4. Chromatographic analysis of organics present in an aqueous phase of the products obtained after thermal treatment of Barzas coal at 475°C suggested that the principal organic components of this phase (its amount was of ~ 3-5% wt.%) were phenol and its methyl and dimethyl derivatives. Their total concentration in CH_2Cl_2 extract exceeded 84.5% by weight.

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