ISSN 1070-4280, Russian Journal of Organic Chemistry, 2015, Vol. 51, No. 12, pp. 1677–1680. © Pleiades Publishing, Ltd., 2015.
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Microwave-Assisted Conversion of Lignin into Aromatic Compounds

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Received September 23, 2015

Abstract—Low-power (≤10 W) microwave radiation considerably reduces the initial temperature in the catalytic hydrocracking of lignin as compared to conventional thermal heating. The microwave-assisted catalytic transformation of lignin at 260–290°C under atmospheric pressure afforded in high yield C_6–C_{10} aromatic and aliphatic hydrocarbons in addition to methoxyphenols and alkylated methoxyphenols. A correlation has been found between the activity of the catalyst (1% Pt/C) and the size of platinum metal particles.

DOI: 10.1134/S1070428015120015

Nowadays, a very important technological and environmental problem is development of methods for utilization of wastes from wood processing industry, including their efficient conversion into renewable energy sources [1]. Lignin is one of the main wood components. The weight fraction of cellulose and hemicellulose in wood amounts to ~70%, and lignin constitutes the remaining ~30%. Lignin contains less oxygen than does cellulose; therefore, it is characterized by a higher heat of combustion (6.3 cal/g). Pyrolysis of lignin involves mainly its charring and tarring and, to a lesser extent, decomposition into compounds with low molecular weight.

A promising renewable energy technology is based on fast pyrolysis with formation of carbon materials [2, 3]. Methods of oxidative gasification of lignin to obtain hydrogen-containing synthesis gas have been reported. Gasification of lignin over Ni/MgO catalysts in supercritical water has been studied in [4] with the goal of obtaining hydrogen. The best results were achieved with the use of 10% Ni/MgO as catalyst at 600°C, but the yield of undesirable carbon residue (coke) was as high as 30%. Among large-scale lignin utilization procedures, only direct nitration with nitric acid, preparation of charcoals by pyrolysis, and simple pressing to fuel pellets are known.

Various ways of lignin conversion into a liquid fuel are explored [5]. Anaerobic pyrolysis and thermal dissolution in organic solvents lead to predominant formation of high-boiling products with increased oxygen content [6]. These pyrolysis products should then be subjected to catalytic cracking and hydrogenation to obtain motor fuel. Hydrogenation of lignin at 350–390°C and a hydrogen pressure of 133–196 atm in the presence of a supported catalyst (cobalt, nickel, ruthenium, platinum, iron, rhenium, palladium, chromium) produces mono-, di-, tri-, and tetraalkylcyclohexanes, cycloheptane, C_7–C_{10} alkanes, alkylbenzenes, and other compounds [7].

Low-molecular-weight Alcell® lignin which is soluble in acetone and more readily degradable was used as raw material to obtain aromatic hydrocarbons by cracking over HZSM-5 zeolite catalyst [8]. The highest yield of liquid products (43%) was achieved at 550°C when an acetone–lignin mixture (2 : 1 by weight) was supplied at a weight hourly space velocity of 5 h^{-1}. The liquid products contained mainly toluene (36.7%), xylenes (33%), and benzene (9.4%).

Our previous studies [9] have shown that microwave activation of hydrogenation–dehydrogenation of polycyclic hydrocarbons, e.g., reversible hydrogenation–dehydrogenation of terphenyl, over noble metal-based catalysts considerably enhances the catalytic activity (by a factor of 3–5) and reduces the initial temperature by 100–200°C [10]. The crucial advantage of the energy transfer via microwaves compared to thermal heating is fast energy penetration into the bulk material (catalyst) that absorbs microwave radiation. Hydrogenation of lignin is a high-temperature process. We previously [11] determined the series of supports and catalysts capable of being heated by low-power microwaves (≤10 W) to high temperature necessary for the conversion of methane into aromatic hydrocarbons. This series includes various metals (Pt, Ni) applied to carbon supports, metal carbides (TaC, WC), and Pt/TiO_2.

In this work we examined transformations of high-molecular-weight technical (hydrolysis) lignin over catalysts that can be heated by low-power microwaves (≤10 W). When microwave-heatable Pt/C was used, the reaction mixture was heated in a stream of nitrogen only to 140–145°C (Fig. 1a). Nitrogen supply was then replaced by hydrogen (15 mL/min), and the hydrocracking was performed over a period of 40 min (Fig. 1b).

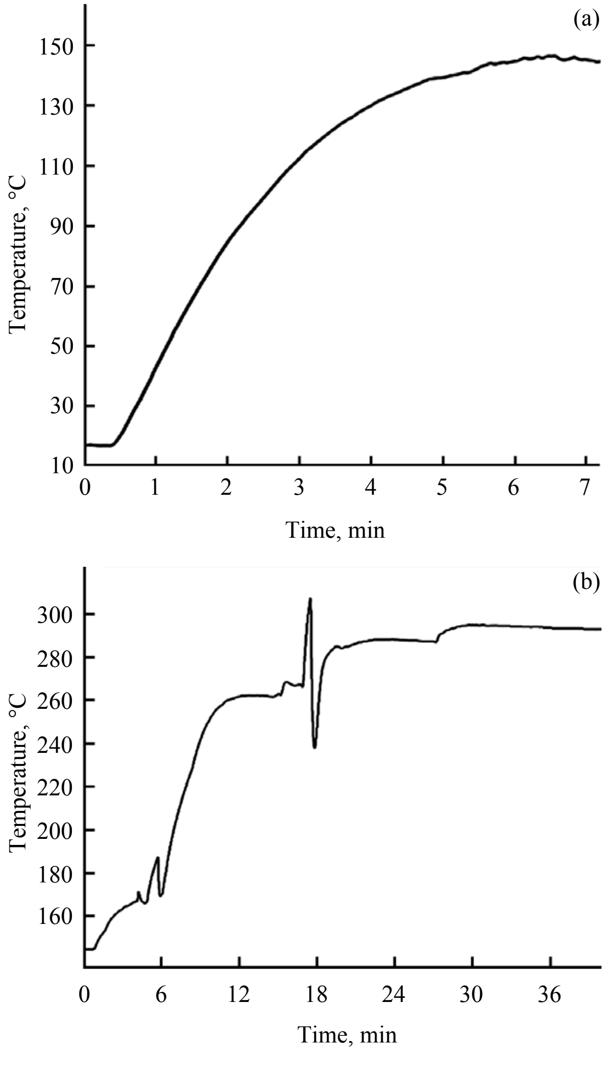

Fig. 1. Temperature profiles of the reaction bed (lignin + Pt/C, sample *1*) under microwave irradiation (5.7 GHz, 10 W) (a) in a stream of nitrogen and (b) after replacement of nitrogen by hydrogen.

Figure 1b shows that the temperature of the reaction mixture (lignin + catalyst) preliminarily heated in a stream of nitrogen considerably increases (by 140–160°C) after hydrogen supply for 15 min (Fig. 1b). This unambiguously indicates transformation of lignin via exothermic catalytic process. In the course of hydrocracking (40 min) the temperature of the reaction bed stepwise increased from 265 to 290°C with a short burst to 310°C at the 18th minute (Fig. 1b). In a blank experiment (in the absence of lignin), the temperature of the Pt/C bed decreased by 5–10°C after replacement of nitrogen by hydrogen, obviously due to the higher heat capacity of hydrogen. Thus, temperature bursts in the reaction bed provide an additional evidence in support of lignin transformation and accompanying bed compaction.

Figure 2 shows the chromatogram of liquid products of lignin hydrocracking over 1% Pt/C (sample *1*), and the composition of liquid products formed in microwave-assisted lignin hydrocracking at 265–295°C over two different Pt/C samples is given in Table 1. Among the identified hydrocarbons, we detected high-molecular-weight alkyl- and methoxyphenols and alkylbenzenes together with low-molecular-weight C_6–C_{10} aliphatic and aromatic hydrocarbons. The conversion of lignin was 28.2 and 15.6% for Pt/C samples *1* and *2*, respectively.

Table 2 contains the results of our measurements of the dispersity of platinum in samples *1* and *2* [12]. Comparison of the data in Tables 1 and 2 unambiguously shows that the conversion of lignin increases as the size of platinum metal particles decreases.

It is known that lignin conversion over nickel- [13] and rhodium-containing catalysts [14] is accompanied by formation of synthesis gas. Our results demonstrate that microwave-activated hydrocracking of high-molecular-weight lignin effectively proceeds even at a fairly low temperature (260–290°C) under atmospheric pressure. According to [15], selective hydrocracking of low-molecular-weight lignin (depolymerized by alkali) over Pt/SO_4^{2-}/ZnO and Pt/WO_4^{2-}/ZnO with formation of alkylbenzenes, alkylphenols, and alkoxyphenols is efficient only at higher temperature (350–375°C).

Presumably, microwave irradiation of Pt/C catalyst induces local high-temperature (>500°C) heating of

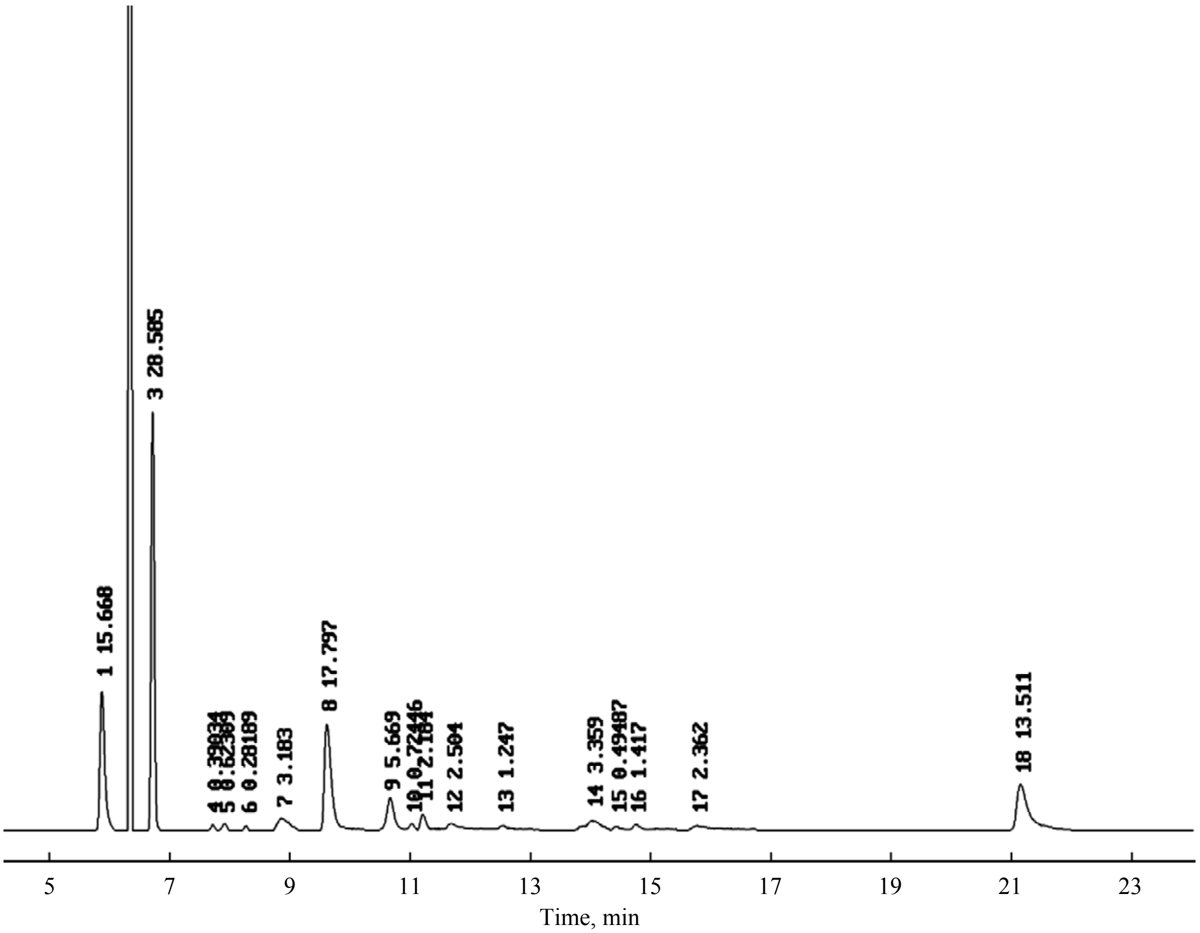

Fig. 2. Chromatogram of the lignin hydrocracking products.

platinum metal particles to generate “hot spots” acting as hydrocracking active sites, which does not affect the measurable mean temperature of the reaction bed (260–290°C). The behavior of hybrid catalysts [16] under microwave activation and the corresponding catalytic transformations constitute a very interesting subject for further studies.

Thus, microwave-assisted hydrocracking of lignin at 260–290°C with a conversion of up to 30% leads to the formation of lower (C_6–C_{10}) aromatic and aliphatic hydrocarbons in addition to high-molecular-weight alkylated methoxyphenols (lignin structural fragments). The activity of the catalyst (1% Pt/C) is related to the size of platinum metal nanoparticles; the catalyst with smaller platinum particles is more active in the hydrocracking of lignin.

EXPERIMENTAL

Preparation of Pt/C catalyst. Sibunit with a grain size of 0.1–0.25 mm was used as carbon support.

Sample 1 was prepared by platinum deposition onto the support surface. For this purpose, a 1 M solution of sodium carbonate was added at 19°C to a 0.001 M

Table 1. Composition (wt %) of liquid products of lignin hydrocracking over 1% Pt/C

Product[a]	GC peak no.[b]	Sample *1*	Sample *2*
C_6–C_8 hydrocarbons	1, 3–6	45.8	26.2
Cyclohexane (solvent)	2	Not determined	
Phenol	7	3.2	4.6
Ethylbenzene	8	17.8	12.3
1-Ethyl-4-methylbenzene	9	5.7	3.8
Butylbenzene	11	2.2	4.2
2-Methoxyphenol	14	3.6	5.2
2-Methoxy-4-propylphenol	18	13.5	15.6
Unidentified	Others	8.2	28.1

[a] Lignin conversion, %: 28.2 (*1*), 15.6 (*2*).

[b] See Fig. 2.

Table 2. Average size of platinum metal particles in samples *1* and *2* of 1% Pt/C, determined by the CO titration and X-ray powder diffraction methods

Sample	Dispersity, CO/Pt	Mean Pt particle size, nm	Pt particle size (XPD), nm
1	0.66	2	Amorphous
2	0.24	6	7.5

solution of H_2PtCl_6 until pH 6.9, a required amount of Sibunit was added, and the resulting suspension was vigorously stirred for 1 h at 19°C and for 1 h at 80°C. The mixture was filtered, and the catalyst was repeatedly washed with distilled water on a filter, dried in air for 2 h at 90°C, and activated in a stream of hydrogen (180°C, 1 h; Table 1).

Sample 2 was prepared by adsorption of H_2PtCl_6 from a 0.0004 M aqueous solution on Sibunit preliminarily subjected to oxidative treatment as described in [13]. The catalyst was filtered off, repeatedly washed with distilled water on a filter, dried in air for 2 h at 90°C, and activated in a stream of hydrogen first for 1 h at 150°C and then for 2 h at 250°C (Table 1).

The completeness of platinum deposition (adsorption) was checked by qualitative tests with potassium iodide (sensitivity 2 μg/mL).

Hydrolysis lignin manufactured by the Krasnoyarsk Hydrolysis Plant (moisture content 60%, grain size 0.5–1 mm) was preliminarily dried for 6 h at 120°C in a drying box.

Hydrocracking of lignin. Dried lignin, 200 mg, and Pt/C catalyst (sample *1* or *2*), 100 mg, were mixed in a ball mill, and the mixture was placed into a flow reactor (a quartz tube 7 mm i.d.) to form a 1.0-cm bed. The reactor was placed into a microwave resonator (power 10 W, frequency 5.7 GHz) and heated at 265–290°C (reaction mixture temperature) in a stream of hydrogen at a flow rate of 15 mL/min. Cyclohexane was introduced into the stream of hydrogen to remove heavy liquid hydrocarbons formed during the process. For this purpose, before feeding into the reactor, hydrogen was bubbled through a layer of cyclohexane maintained at 30°C. Liquid products were trapped in a receiver cooled to 0°C. The conversion of lignin was determined from the weight loss after the process.

The products were analyzed on a Kristallyuks chromatograph equipped with a flame ionization detector; SE-30 capillary column, 25 m; oven temperature programming from 70°C (4 min) to 180°C at a rate of 8 deg/min.

This study was performed under financial support by the Russian Science Foundation (project no. 14-50-00126).

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