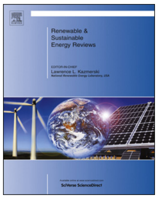
Renewable and Sustainable Energy Reviews 57 (2016) 1008–1024

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Carbon adsorbents from industrial hydrolysis lignin: The USSR/Eastern European experience and its importance for modern biorefineries

Mikhail L. Rabinovich [a,*], Olesya Fedoryak [b], Galina Dobele [c], Anna Andersone [c], Barbara Gawdzik [d], Mikael E. Lindström [e], Olena Sevastyanova [e,f,**]

[a] *A.N. Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[c] *Latvian State Institute of Wood Chemistry, Riga, Latvia*
[d] *Maria Curie-Skłodowska University, Faculty of Chemistry, Lublin, Poland*
[e] *Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden*
[f] *WWSC Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden*

ARTICLE INFO

Article history:
Received 18 January 2015
Received in revised form
30 October 2015
Accepted 18 December 2015

Keywords:
Hydrolysis lignin
Carbon adsorbents
Collactivite
Thermal transformation
Phosphoric acid activation
Alkaline activation
Application

ABSTRACT

This paper reviews the origin, distribution and composition of hydrolysis lignin, a large-scale by-product of the hydrolysis industry that operated in the Soviet Union and several eastern European countries from 1930s to the end of 1990s. The fundamental and industrial aspects of the production of various types of powdered and granular carbon adsorbents from hydrolysis lignin are considered through the prism of future large-scale production of biofuels and platform chemicals from renewable lignocellulosic resources. The advantages and drawbacks of hydrolysis lignin as a feedstock for the production of carbon adsorbents are compared with other types of feedstock, and the application of lignin-based carbons is discussed.

Contents

1. Introduction

In recent years, there has been a growing interest in the development of 2nd generation biofuel technologies, as well as in the production of bio-based platform chemicals and commodities from lignocellulosic feedstock. This raises the problem of how to

---

* Corresponding author at: A.N. Bach Institute of Biochemistry, Russian Academy of Sciences, Moscow, Russia.
** Corresponding author at: Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden. Tel.: +46 76 776 27 35.
E-mail addresses: mirabi@mail.ru (M.L. Rabinovich), olena@kth.se (O. Sevastyanova).

http://dx.doi.org/10.1016/j.rser.2015.12.206
1364-0321/

utilize the major by-product, residual lignin, which can constitute up to 40% of the original feedstock on a dry basis (db). The former USSR and some of the Eastern European countries experienced the same problem with their domestic wood hydrolysis industry for more than 75 years. Before and during World War II, both Germany and the Soviet Union exploited acid hydrolysis of wood in order to produce fuels and chemicals. In Germany, during the period 1930–1945, both percolation hydrolysis of wood using dilute H_2SO_4 at elevated temperatures and pressures (the Scholler process) and low-temperature hydrolysis using concentrated HCl (the Bergius process) were used. However, these processes were discontinued soon after the end of the war due to their economic unreliability. Similar processes that were tested after the war in the USA and Japan were also abandoned for this reason [1,2].

After World War II and until the beginning of the 21st century, acid hydrolysis of wood and agricultural residues for the production of ethanol, fodder yeast, hexose and pentose sugars and their derivatives (e.g., furfural and xylitol) had industrial applications only in the former USSR and Bulgaria. It was based mainly on percolation hydrolysis using diluted H_2SO_4, which was developed in the former USSR and used from the 1930s to the 1990s, although some semi-industrial facilities for wood or agricultural residue hydrolysis using concentrated HCl were also used during this period (e.g., Kansk Plant in Siberia) [2]. Wood hydrolysis facilities were built in both the northern and southern European regions of Russia, as well as in Siberia and the Russian Far East. Other hydrolysis plants in the former USSR were located in Ukraine, Belarus, Uzbekistan, Kazakhstan, Moldova and Lithuania. Two wood hydrolysis plants were also built and operated in Bulgaria [2]. In addition, during the 1950s and 1960s, China and North Korea built their own hydrolysis plants based on Soviet technology [2–4]. A comprehensive review of the main objectives of the acid hydrolysis industry, as well as of the feedstocks and processes used therein and of the range of products (commodities and fine chemicals, including pharmaceuticals) manufactured thereby, may be found elsewhere [1].

All or most of these facilities produced substantial amounts of excess lignin, so-called "hydrolysis lignin" (HL). Indeed, by the 1980s, the aggregate amount of excess HL reached 1.5 million tons (db) annually. This continued right until the complete collapse of the acid hydrolysis industry, which was caused, first, by the drop in the crude oil price in the mid-1980s, and, subsequently, by the disintegration of the USSR and the resulting cessation of state subsidies.

The high moisture content of HL, along with the presence of residual acid, the complexity of its composition and its extreme heterogeneity, hampered the utilization of HL as a fuel. Consequently, excess HL was deposited in lignin dumps near the hydrolysis plants, resulting in smoldering fires and severe environmental pollution. Currently, the largest lignin dumps are located in Russia: Onega, Segezha, Arkhangelsk, Syktyvkar, Kirov, Gubakha, Lobva, Tavda, Ivdel, Manturovo, Shumerlya, Krasnodar, Kropotkin, Ust-Abakan, Zima, Biriusinsk, Tulun, Bratsk, Kansk, Krasnoyarsk, Khor and Lesozavodsk. These dumps have accumulated an aggregate of approximately 30 million tons of HL (db). In addition, approximately 3 million tons have accumulated in Belarus (Bobruisk and Rechitsa), 2–3 million tons have accumulated in Ukraine (Zaporizhia and 7 other smaller plants,), and smaller quantities have accumulated in Moldova (Beltsy and Bendery), Uzbekistan (Fergana, Andizhan and Yangiyul) and Kazakhstan (Shymkent). The Nancha hydrolysis plant in Heilongjiang province in China deposited nearly 10,000 tons of HL annually until the 1990s, in addition to using all of the adjacent forest resources. At least two lignin dumps are currently situated in the European Union, namely, Kedainiai in Lithuania and Razlog in Bulgaria.

Most of the proposed techniques for the utilization of HL considered it as a substitute for other feedstock. In most cases, however, HL could not compete successfully with the original feedstock. One of the few promising avenues for the commercialization of HL was the production of various adsorbents, including activated carbons (AC), for environmental and other applications. Indeed, the future production of such adsorbents could be a significant boost for the lignocellulose biorefinery industry, of which HL is a large-scale by-product.

There have been relatively few articles published in English concerning the preparation of AC from lignin. Moreover, the only English-language paper to have reviewed the work done on the use of lignin and of lignin-based chars and activated carbons as adsorbents was published by Carrot SPJM and Carrot MMLR in 2007. That paper covered the literature that had been published in English during the preceding few decades [4]. However, carbonization and the production of AC from HL were studied in detail in the former USSR, including at the industrial level. This paper attempts to uncover and summarize the research efforts (most of which were not digitized and, therefore, were previously inaccessible by western readers) on the production of carbon adsorbents from HL that were conducted in the former Soviet Republics and Eastern European countries during the period between 1930s and 1990s.

2. Structure of HL and main types of AC derived therefrom

Although the majority of industrially produced hydrolysis lignin was obtained by the percolation hydrolysis [2] of softwood or hardwood, other types of industrial HL residues have also been tested as a feedstock for the production of activated carbon (AC). HL by-products from the percolation hydrolysis of wood in an acidic medium at 150–190 °C and a pressure of 0.8–1.0 MPa are characterized by their varying composition. They contain up to 60–70% moisture at pH 1.5–2, which corresponds to a residual H_2SO_4 content of 0.4–2.4%, and 48–72% (db) Klason lignin. Researchers have different opinions on the structure of the lignin component of HL. Chudakov considers the lignin from percolation acid hydrolysis to be an excessively cross-linked and condensed product, based on its significant oxidation and the inability of its major fraction to dissolve or swell in any solvents without preliminary chemical destruction [5]. Other researchers emphasize the presence of a low-molecular-mass fraction in the lignin component, which evidences the substantial weakening of the lignin-carbohydrate and intramolecular C–O–C-ether bonds in the original lignin macromolecular network [6].

The lignin component of percolation HL differs considerably from that of native lignins. Prolonged high-temperature acid hydrolysis results in a substantial reduction of lignin reactivity, the disappearance of carbonyl groups and the formation of C=C bonds in the α,β-position [7]. High-temperature acid hydrolysis of the lignin–carbohydrate bonds also leads to the formation of free radicals, which may, in turn, initiate polymerization reaction. This results in a network structure that is typical of HL (Fig. 1). In particular, phenoxy and quinomethide radicals initiate the repolymerization and formation of a *de novo* 3-D network in the HL. The free radical concentration typically varies between 10^{16} and 10^{18} spin/g HL, increasing with the intensity of the thermal treatment. However, most of these free radicals are stable for years because of the steric "cage" effect. As a result, they are not easily involved in radical-initiated chemical conversions, such as copolymerization or oxidative depolymerization, whether in the lignin dumps or during the technical processes. The simultaneous presence of quinoid and free phenolic groups in the structure of HL may indicate that HL has both acceptor and donor properties in