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Good real world example of wood-based sustainable chemistry

D. Grinshpan*, T. Savitskaya, N. Tsygankova, S. Makarevich, I. Kimlenka, O. Ivashkevich

Belarusian State University, Leningradskaya str., 14, 220030 Minsk, Belarus

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ABSTRACT

One of the principles of Green chemistry is the usage of biomass instead of crude oil for the production of chemicals and chemical goods. Wood refers to the term biomass along with agricultural residues, energy crops, and the biogenic part of waste such as solid municipal waste, landfill, sewage gas and farming waste. Wood is mainly composed of cellulose, lignin and hemicelluloses. Cellulose is the main component of wood and lignin is the main by-product of cellulose extraction. Our green approach to both of these polymers resulted in creating a new process for hydrocellulose fiber production and a new sorbent for oil spills removal based on hydrolysis lignin. It is worth pointing out that our approach provides the use of two main wood components in the frame of "cradle to cradle" cycle (Fig. 1) that supports the circular economy concept for research and process development (Clark et al., 2016).

1. Introduction

Cellulose is the world's most important biopolymers. The renewable feedstock for cellulose is biomass. *Cellulose* is the main structural material in plant cell wall (Gardner and Blackwell, 1974), which contributes 45% of wood mass. The less abundant components are hemicelluloses and lignin; the former takes about 35% in hardwoods and 25% in softwoods, while the latter takes up 21% in hardwoods and 25% in softwoods respectively. It constitutes around 1.5×10^{12} t of the total annual biomass production and approximately 2% of it is used for the production of cellulose regenerated (hydrocellulose) fibers and films (Klemm et al., 2005). Cellulose regenerated fibers are assigned to the cellulosic fibers along with cotton fibers. The former are called "man-made fibers" and the latter – "natural fibers". Man-made cellulosic fibers are extremely sustainable fibers (Haemmerle, 2011). In comparison to cotton, they have some important assets: no arable land is necessary. The trees for the pulp production are growing in forests or on marginal. They require less water consumption, no input of pesticides and fertilizers. Man-made cellulosic fibers are really ecological fibers: the substitution of cotton by man-made cellulosic fibers is an important step in order to protect our environment.

An irony of the state-of-art in the manufacture of man-made fibers is that one of the cleanest fiber types, i.e. hydrocellulose fiber, is produced by not environmentally friendly method in spite of the fact that industrial methods are modified and the alternative ones are still proposed (Regenerated Cellulose Fibers and Woodings, 2001; How It Works, 2003; Sixta et al., 2015).

We started green strategy for the hydrocellulose fibers production in the late 80's before P. Anastas and J. Warner enunciated twelve principles of Green chemistry (Anastas and Warner, 1998). Since that, three processes have been developed by the team of the Laboratory of cellulose solutions of the Belarusian State University (Grinshpan et al., 1994, Grinshpan, Gonchar et al., 2011; Grinshpan, Savitskaya et al., 2011; 2014b). They based on dimethylformamide-dinitrogen tetroxide system (*Camilon* process) (Grinshpan, Savitskaya et al., 2011; Chegolya et al., 1989), zinc chloride aqueous solution (Grinshpan, Savitskaya et al., 2011; Grinshpan et al., 1993) and orthophosphoric acid aqueous solution (*Greencel* process) (Grinshpan, Gonchar et al., , 2011, Grinshpan et al., 2014b). As a result we observe the evolution of hydrocellulose fiber production processes, where each of three ones gets greener and greener every step of the way. The development of two processes has been stopped at present because of the only Greencel process has the real prospect as a cleaner production. Meanwhile this article describes them all.

Lignin is one of the three major compounds of biomass along with cellulose and hemicelluloses. Biosphere has an estimated 3×10^{11} metric tons of lignin with a 2×10^{10} metric tons annual biosynthesis rate (Kaplan, 1998). Lignin is produced as a by-product at the production of bulk chemicals like cellulose (pulping process) and ethanol (hydrolyzed alcohol) (Vanholme et al., 2010). Lignin, which contains no sugar units, is separated by percolation acid hydrolysis by diluted sulfuric acid from the cellulose and hemicelluloses, which do contain sugar units. Hydrolysis lignin (Rabinovich, 2014) is still in its solid form after lignocellulosic ethanol production (Vishtal and

Abbreviations: PAN, poly(acrylonitrile); PAA, polyacrylicacid; PVAl, poly(vinylalccohol); PVC, poly(vinylchloride; CPVC, chlorinatedpoly(vinylchloride); PA, poly(amide); PVAc, poly(vinylacetate); PMMA, poly(methylmethacrylate); SNR, syntheticnitrilerubber; MCC, monocarboxylcellulose

* Corresponding author.

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Kraslavski, 2011;) and has various applications: in energy sector (for the production of briquettes, pellets, pyrolysis bio-oil and fuel gas); in chemical industry (as a sorbent for purification of industrial effluents); in agriculture (for the organic-mineral fertilizers and herbicides production) (Telysheva and Pankova, 1978; Siurus, 2012; Botlovski, 2014), and so on (Vishtal and Kraslavski, 2011), including the production a high value product levoglucosenone and cleaner lignin from waste hydrolysis lignin (De Bruyn et al., 2016).

Decay resistance of lignin is based on its initial role in nature to protect cell wall polysaccharides from microbial degradation. For this reason, it is not surprising that the biodegrability of lignin appears to be quite low, and the only palisade wood-destroying fungi causing the white rot (Coriolus versicolor, Fomesfomentarius) and some nesting basidimycetes (Collybria, Marasmius, Mycena) activated the degradation of lignin (Dzedulya, 2001).

Among the numerical trends of lignin uses, we have found a niche namely the process of drying hydrolysis lignin. It has been developed for the production of new sorbent. Hydrolysis lignin hydrophobized by drying in a special way has demonstrated a good sorption capacity for oil spills removal and utilization of oil products waste. The transformation of liquid oil product into the solid mass after the contact with lignin sorbent opens its further usage. Such solid composite fuel has high combustion heat value that gives a second life for two environment hazardous wastes: lignin and oil products (Grinshpan, Telysheva et al., 2011; Savitskaya, 2012).

Dealing with hydrocellulose fiber production process and lignin recovery we have developed the idea of hydrolysis lignin usage for the production of combined organic-mineral fertilizer based on the inorganic salts of the hydrocellulose fiber coagulation bath mixed with lignin. First positive results on the agricultural plants productivity increase have been reached.

This article aims to demonstrate the real implementation of green chemistry principles in one laboratory that has resulted in the creation of green processes and eco-friendly products. The article reveals new research results and a comprehensive outline of the research process. This is the first time we have outlined our more than 30 years of expertise from the point of view of Green chemistry principles. When preparing this article we strived for the potential interest in this subject among the researches working in the area of natural polymers. We think our consecutive approach for cellulose and lignin, both of which are the components of such inexhaustible bioresource as wood, would be interesting for the proponents of Green chemistry. It follows from Fig. 1 that this approach provides the use of two main wood components in the frame of “cradle to cradle” supporting the circular economy concept for research and process development (Clark et al., 2016).

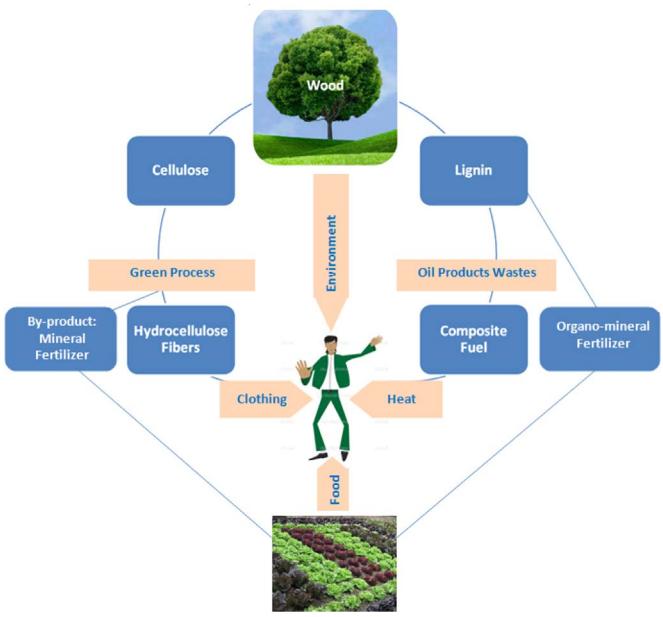

Fig. 1. Research Strategy from the Continuous Life Cycle Point of View.

2. Cellulose

The historically first *Viscose* process is famous for air and water pollution (Regenerated Cellulose Fibers and Woodings, 2001) and use of harmful carbon disulfide (Toxicological Profile for Carbon Disulfide, 1996). There are different kinds of *Viscose* process, e.g. *Modal* process that is the kind of *Viscose* process with an advanced scale of adapted precipitating bath which guides to fibers with improved properties (higher dry and wet strengths and recovered dimensional stability) (Woodings, 1995). Modern modifications of Viscose process move to the reuse of harmful chemicals rather than discharged to the environment (How It Works, 2003). Nevertheless, it is not very progressive way and *Viscose* process is concerned to be the most harmful in the chemical fiber industry (Slater, 2003).

Several alternative processes have been proposed throughout the last century. Their main advantage is the absence of toxic gases such as CS_2 and H_2S. Parallel to *Viscose* and *Modal* processes one can mention such processes as *Cupro* ([cellulose/solvent $[Cu(NH_3)_4](OH)_2$), *Lyocell* (cellulose/solvent - *N*-methylmorpholine*N*-oxide (NMMO)) (Borbely, 2008), and *Fortisan* (cellulose acetate/solvent - acetone, saponified) which are commercial now (Handbook of Fiber Chemistry, 1998) and differ in dissolving system. A great variety of experimental fibers have been proposed along with the fibers produced in industrial scale. The reason is that the increasing prosperity of the growing population increases the demand of cellulosic textile fibers, which cannot be satisfied by the global growth of cotton and the existing cellulosic fiber capacities. Besides, the detailed analysis of the relatively new processes implemented in industry, e.g. *Liocell*, shows the problems with unsafe side reactions and by-products (Rosenau et al., 2001).

The freshest elaborated fiber is *Ioncell* (cellulose/solvent - ionic liquid) (Cao et al., 2010; Sixta et al., 2015; Michud et al., 2016). *Bocell* (cellulose/solvent - superphosphoric acid) (Boerstoel, 1988), *Carbamate* (cellulose/solvent - NaOH/urea) (Cai et al., 2007; Ruan et al., 2004), *BioCelsol* (cellulose/solvent- Enzyme/NaOH/ZnO) (Martincin et al., 2007), *Du-Pont* (Cellulose acetate/solvent - trifluorthriacetic/ solvent - formic acid, saponified) (O'Brien, 1984), *Micheline* (cellulose/solvent - formic acid/organic solvent and inorganic acid) (Sioumis, 1991) are the experimental hydrocellulose fibers that are at a different distance from the finish today. On the way to the industrial implementation, the most common issues for the new processes are water consumption (Haemmerle, 2011) and solvent recovery (Fernandez et al., 2011).

The development of alternatives to *Viscose* process has led us to real green process of hydrocellulose fibers production based on the aqueous solutions of orthophosphoric acid. Our way to this green technology came through two another alternative technologies based on aqueous and non-aqueous cellulose solutions as well.

2.1. Camilon process: dimethylformamide-dinitrogen tetroxide dissolving system

This process development started in 1986 and finished with a pilot plant process for manufacturing regenerated cellulose fibers (Grinshpan et al., 2003; Chegolya et al., 1989; Grinshpan, Savitskaya et al., 2011). Dimethylformamide (DMF) with 7–17 wt% of dinitrogen tetroxide was used as a solvent for cellulose. 7–8 wt% homogeneous, transparent solutions of cellulose with the degree of polymerization of 560 were prepared at ambient temperature and pressure. The total time for preparing a spinning solution was reduced threefold in comparison with that of normal viscose solutions. A technological