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Fundamental Properties of Nanocellulose

Tsuguyuki Saito, Yuri Kobayashi, Shuji Fujisawa, Chun-Nan Wu and Akira Isogai
The University of Tokyo

Cellulose is the most abundant polymer on earth, and is produced in plant cell walls as highly crystalline microfibrils consisting of fully extended and uniaxially aligned cellulose molecules. These microfibrils have very small widths (3 nm), high aspect ratios (>300), high elastic moduli (110-140 GPa), a low coefficient of thermal expansion (6 ppm K^{-1}), and large surface areas (900 m^2 g^{-1}). Owing to these characteristics, cellulose microfibrils have recently been attracting much interest as structural components in nanomaterials. These microfibrils have the potential to be applied as reinforcements in composite materials and high-capacity supports for catalyst, conducting, and magnetic materials. However, because individual cellulose microfibrils are strongly associated with each other in plant cell walls, it is essential to fibrillate cellulose before new materials consisting of cellulose microfibrils can be developed.

In this context, it has been found that cellulose can be fully dispersed in water as individual microfibrils via the application of a topological surface carboxylation reaction on cellulose microfibrils using 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) as a catalyst. The dispersed microfibrils spontaneously align in water. The integration controls of the self-aligned microfibrils, i.e., careful adjustment of the pH and evaporation of the solvent in the microfibril dispersions, produces a wide range of artificial bulk materials with outstanding properties. Examples include unprecedentedly stiff hydrogels that are free-standing with a water content of 99.9%, ultralow-density, tough aerogels with large surface-areas, and transparent films with exceptionally high oxygen-barrier properties. These materials are expected to further develop as robust frameworks of polymer nanocomposites or high-capacity supports of catalysts and the other functional materials.

Basic Items of KP Bleaching

Makoto Iwasaki
MIP Consultant Office

This article widely describes about change of equipments for KP bleaching, trend of the operation, bleaching chemicals and the chemistry, finally topics related to KP bleaching.

The Latest Ozone Generation Technology

Shinsuke Goto, Hajime Nakatani and Yoshiaki Odai
Department 1, Kobe Works Public-use Systems, Mitsubishi Electric Corporation

Ozone is made of three oxygen atoms which has strong oxidizing power. In the paper mill industry, ozone is used for pulp bleaching. However, since lots amount of ozone production is required for pulp bleaching, the increase in electric power cost and enlargement of an ozone generator were challenges to be achieved. Since improvement in efficiency of ozone generation and downsizing of the ozone generator were actualized, now our solution is introduced herein.

The improvement in efficiency of ozone generation was focused attention on discharge gap length. By “Narrow gap" which shortens discharge gap length, the energy distribution of the electron has been shifted to the higher distribution.

As the result, since the low-energy electrons which decompose ozone decrease and the high-energy electrons which generate ozone increase, the improvement in efficiency of ozone generation has been achieved. The specific power consumption of the ozone generator are reduced by about 27% at ozone concentration 12wt% from conventional type.

Downsizing of the ozone generator was focused attention on the increase in the discharging area and on the increase of the amount of ozone production per specific discharging area in the same ozone generator (it means the same diameter of the shell). By adoption of the small electrode whose diameter is smaller than the conventional one, the discharging area was increased by 4 times. Moreover, the amount of ozone generation per specific discharging area was increased twice by "Narrow gap".

As the result, in the case of the same ozone generator (the same diameter of the shell), the total amount of ozone production is risen by 8 times than the conventional type and on the one hand, compared with the same ozone production, the ozone generator (the diameter of the shell) becomes more compact to $1/\sqrt{8}$ ($\fallingdotseq 1/2.8$) of the conventional type.

Optimization of Operating in Lime Kiln

Yasuhiro Ogawa
Tomioka Mill, Oji Paper Co., Ltd.

At Tomioka mill, Oji Paper, in a lime kiln, although heavy oils, plastics, and biogases are

used as combustion fuel, the fuel cost of the kiln is in an aggravation tendency by the jump in a heavy oil price.

Then, Taiheiyo Engineering Corporation, which has implemented the energy conservation measures in cement kilns for years, was invited as operation consultant, and the technique was made to apply to the lime kiln.

Although three kinds of fuel were throw in with the individual burner, the burner which united the injection nozzle, TMP burner（Taiheiyo Multi-Purpose burner） was introduced in March, 2010. In this time, the lime kiln equipment was totally caught in addition to the burner, and the following measures were implemented.

1) Stabilization of the filling factor of sludge in the lime kiln
2) Adjustment of a flame
3) Optimization of the lime layer thickness in the lime cooler
4) Adjustment of the injection air content to the kiln
5) Optimization of the oxygen concentration at the kiln inlet housing

As a result of adopting above mentioned measures, we achieved 6% reduction of the fuel consumption.

The Measure against Operational Improvement of Green Liquor Clarifier of Causticizing Process

Hiroshi Fujita
Niigata Mill, Hokuetsu Kishu Paper Co., Ltd.

The production facility of Niigata Mill, Hokuetsu Kishu Paper Co., Ltd has digesters of two series, washing and bleaching equipments of three series, and causticizing equipments of three series. However, since it has only green liquor treatment equipments of two series, the load more than a design throughput has been hung. Since it is electrical overload operation, poor sedimentation in a green liquor clarifier tank takes place. Suspended solid in clear green liquor may go up by 4 times the standard value. If poor sedimentation in a green liquor clarifier tank takes place, a lime kiln-causticizing process will become out of condition by poor drying of a lime mud filter and change of the temperature profile in a lime kiln.

Then, cause investigation with poor sedimentation with a green liquor clarifier tank was conducted. And poor sedimentation of a green liquor clarifier tank has been improved by performing operation measures against an improvement, such as adjustment of green liquor concentration.

Ｔhe Evaluation of the Hydrogen Peroxide Addition at EP Stage by Using Catalase

Yoshiaki Mase
Hachinohe Mill, Mitsubishi Paper Mills Limited

In Hachinohe mill, there are three bleaching lines of kraft pulp. No.3 BKP line whose capacity is 850ADt/d is the biggest line in this mill. Bleaching sequence is A-D0-EP-D1 equipped with diffusion washer.

At No.3 BKP line, we bleached pulp made from several kinds of hard wood chip having different bleaching property. In some cases, both addition of hydrogen peroxide at EP stage and of chlorine dioxide at D1 stage unusually increase. Chlorine dioxide may be consumed by the residue of hydrogen peroxide, so bleaching efficiency would be reduced.

In this paper, we introduce the method of evaluation by using the specificity and selectivity of catalase in order to optimize the residue of hydrogen peroxide at EP stage.

Operational Improvement by Retrofit of Kraft Pulp Fiber Line

Tetsuya Okamura
Kraft Pulp Div., Mishima mill, Daio Paper Corporation

Hardwood fiber line in Mishima mill had increased and extended step by step with expansion of paper machines. The total energy cost was pushed up because of the increased number of equipment and the pulp transportation distance.

On the other hand, the basic density of wood chip became lighter using of Eucalyptus nitens and Acacia, and we decided to retrofit our line to get much more production.

Our retrofit concept of Kraft pulp line was as follows;

1） Production increase
2） Cooking facilitation of a wood chip with a low basic density
3） Energy efficiency improvement by shortening the transportation distance, enlargement of equipment and decreasing the number of it
4） Quality improvement of pulp (reduction of dirt content, stability of pulp strength).

After retrofit, we achieved the production of 1,600 tons/day (100 tons/day of increase), more usage of the low basic density of wood chip, reduction of energy and bleaching cost and the improvement in pulp quality.

Optimization of Operating Condition for Dissolving Kraft Pulp

Takehiro Kojima
Kushiro Mill Production & Plant Engineering Dept., Nippon Paper Industries Co., Ltd.

Rayon attracts growing attention due to demand growth in south eastern Asia and in China recently. Rayon is made from cotton linter and dissolving pulp. While supply of cotton linter is greatly affected by climate, dissolving pulp process can provide stable supply. Demand of dissolving pulp is expected to be stable in the future. Dissolving pulp has been produced by Sulfite process. Since there was a limitation on wood species for Sulfite process, new technology was developed to produce dissolving pulp by continuous Kraft process.

Decision was made to produce the world first SW dissolving Kraft pulp utilizing continuous Kraft process. Construction was completed in October 2012 then commercial production commenced in March 2013.

This report shows optimization of operating condition for dissolving kraft pulp.

Operation Experience of MVR Pre-Eva

Hideaki Suzuki
Sendai Mill, Chuetsu Pulp & Paper Co., Ltd.

In Chuetsu Pulp, Sendai Mill produces HW pulp with continuous digester line and SW pulp with batch digester line.

The weak black liquor dry solids from the continuous digester to main evaporation plant is around 20 DS % with Pre-Evaporator (Pre-Eva) using the flash steam from the digester extraction as heat source.

On the other hand, around 13DS% SW black liquor directly goes to the main evaporator because of no Pre-Eva in the batch digester.

Sendai mill has been increased SW pulp production since 2009. Because of the pulp production increase, the main evaporation plant became overloaded.

Pre-Eva with flash steam from continuous digester has been introduced to Japanese mills. In food processing industry, electricity (compressor) has been used to evaporate the product because such steam would not be so available in the food processing mills.

Sendai mill has recently introduced vapor recompression pre-evaporation plant to the black liquor from SW batch digester to decrease steam consumption of the main evaporation plant as cost saving.

There are no references in Japanese paper pulp industry for vapor recompression evaporator with compressor which has been introduced to the food processing industry. Chuetsu Pulp decided to introduce Andritz Mechanical Vapor Recompression (MVR) Evaporator for Sendai

Mill because Andritz MVR has many references for black liquor pre-evaporation plant all over the world.

This paper explains the general description of MVR plant and the operation experience.

The Production Method of the Viscose Rayon Manufactured Using Dissolving Pulp

Ko Tokuda
Omikenshi Co., Ltd.

The reaction was invented viscose of the cellulose in the U.K. in 1982. It is produced approximately 4 million tons now in the world. It is as follows about the manufacturing method of the viscose rayon. Dissolving pulp is used for the cellulose materials of viscose. Pulp is immersed in sodium hydroxide solution and it is made alkali cellulose. Subsequently, carbon disulfide is made to react to alkali cellulose, and cellulose xanthate is produced. And a dilute alkali solution is added to cellulose xanthate, and it is made to dissolve in it. This solution is called viscose.

Viscose rayon is produced by carrying out solidification reproduction of this viscose.

Viscose rayon is used for clothing, industrial materials, and paper making. Moreover, functional rayon with a special function is produced by adding functional materials to viscose.

The Latest Trouble and the Solution at Pulping Process
—Improvement of Productivity and Quality When Using Acacia Tree—

Masayuki Murano
PULP&PAPER INDUSTRIES DEPARTMENT, INTEGRATED TECHNOLOGY GROUP,
CHEMICAL DIVISION, KURITA WATER INDUSTRIES LTD.

Concerning the environment of the Earth, more and more acacia is used as pulping raw material. Acacia tree has high content of lignin and fatty acid, which will cause various operation trouble much frequently then the other hard wood tree. The troubles include scaling by calcium oxalate, pitch by fatty acid, and poorly-washing efficiency by foaming, and cause both productivity decline and quality drop.

The chemicals such as scale inhibitor, pitch controller and anti-foaming agent are applied to solve these troubles. The scale inhibitor, which works in low pH range is applied for calcium oxalate. The pitch controller can dissolve and disperse metal salt of fatty acid. The cause of poorly-washed pulp is air bubble in pulp slurry, and a proper defoamer can increase dehydration. An improved dewatering can decrease the residue of lignin and fatty acid carry over to latter

process, which will improve the oxygen delignification, reduce bleaching agent, and preventing from scaling or pitch troubles.

Introduction of the Latest DIP Technology

Takanori Goto
Research & Development Dept., Voith IHI Paper Technology Co., Ltd.

A DIP production process is a treasure of cost down - raw material, energy, and chemical costs are variable by the technology of each component. In this paper, we will introduce latest DIP technologies related to each component and system.

Chemical-Mechanical Pulps From Eucalyptus and Their Comparison with Eucalyptus Chemical Pulps

Toshio Okunishi
Andritz K.K.
Eric C. Xu
Andritz Pilot Plant/R&D laboratory
Gary Harris
Andritz Ltd.
Paulo E. Galatti
Andritz Brazil Ltda.
Dieter Teubner
Andritz AG

This paper present recent developments in chemical-mechanical pulping and examines the latest pulping technology, P-RC APMP (Preconditioning followed by Refiner-Chemical treatment - Alkaline Peroxide Mechanical Pulping). The P-RC APMP process is based on peroxide bleaching chemistry, lignocellulose chemistry and refining mechanism. To ensure chemical and mechanical efficiency, the P-RC APMP uses two step chemical addition, first a mild alkaline-peroxide preconditioning of the chips, and second the addition of peroxide bleaching chemicals in refining, so that bleaching occurs both during refining and in a high consistency retention step following primary refining.

The application of the P-RC APMP process to various South American eucalyptus wood species was investigated. Pulps produced were compared with other pulps currently available in the market for various applications. The result showed that eucalyptus P-RC APMP pulps have

papermaking properties comparable to, or better than HWD market BCTMP pulps from North American wood species. When compared with Eucalyptus chemical pulp, the P-RC APMP pulps had higher bulk and higher light scattering at the same tensile index. The higher bulk renders this new process and attractive alternative for the utilization of eucalyptus for many paper and board applications.

Valmet Biorefinery Technology

Hiroshi Yamashita
Sales Group, Pulp & Energy, Valmet K.K.

The promotion of biomass is considered a way of creating a sustainable society for the future. We have been recently facing several challenges such as climate change, increase need for energy, energy security and so on. Then it is expected that the biorefining could be one of the promising solutions. On the other hand, the key factors to expand biorefining are cost efficiency and energy efficiency. Valmet has been developed several refining technologies about biomass. We believe that Valmet biorefinery technologies enable mills to install biofefining and creates new valuable products for mills.

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Photocatalytic Mechanism of Artificial Zeolite Containing Titanium Dioxide

Satoru Fukugaichi
Ehime Institute of Industrial Technology
Teruo Henmi and Naoto Matsue
Faculty of Agriculture, Ehime University

We have already reported the synthesis of an artificial zeolite containing TiO_2 particles (AZT) from paper sludge ash that has a high concentration of TiO_2 (PS ash). This AZT has been able to reduce acetaldehyde gas under UV irradiation. In this study, we investigated the mechanism of the acetaldehyde reduction by X-ray fluorescence, X-ray diffraction, scanning electron microscopy (SEM), BET specific surface area measurements and acetaldehyde decomposition experiments. Acetaldehyde decomposition experiments showed that the AZT had photocatalytic activity, whereas PS ash showed no activity, although TiO_2 particles were present in both. SEM analysis of AZT showed that the TiO_2 particles were closely bound to the zeolite crystal. A zeolite containing TiO_2 (ZT) was prepared through synthesis of zeolite in the presence of TiO_2, and SEM observation revealed a composite structure with TiO_2 particles embedded into large

zeolite crystals. The ZT had higher photocatalytic activity toward acetaldehyde than did the physical mixture of zeolite and TiO_2. The close association of zeolite and TiO_2 that occurs during the synthesis of the zeolite in the presence of TiO_2 might support the transfer of acetaldehyde molecules from zeolite to TiO_2. We conclude that AZT showed photocatalytic activity because of binding of zeolite to the TiO_2 particles. We show that the binding of TiO_2 and zeolite is an important process contributing to the photocatalytic activity of these materials.