Application of Enzymatic Hydrolysis for the Yield Optimization in Froth-Flotation of ONP

JEONG-YONG RYU*, BONG-KEUN SONG† and JAE-KWANG SONG‡

*Principal Research Scientist, †Principal Research Scientist, ‡Senior Research Scientist
Korea Research Institute of Chemical Technology, Dae-Jeon, Republic of Korea
jyryu@krict.re.kr

ABSTRACT

Although cleaner and cheaper deinking of ONP could be performed at the neutral or low alkaline condition, excessive loss from froth-flotation is unavoidable and so reduction of alkali or caustic soda dosage sacrifices recycling yield. Now the new trade-off regarding alkali dosage versus flotation yield is urgently required in order to set the optimized neutral or low alkaline deinking process of ONP.

Lipase from *Thermomyces Lanuginosus* has an effect on desizing and deacetylation reaction and it could be applied to the stock of pre flotation secondary stage in order to reduce the flotation reject without the sacrifice of optical properties of flotation accepts. Instead of inorganic base, lipase could be applied as a biochemical catalyst for the selective modification of valuable hydrophobic particles in deinking stock, for example cellulose fines and inorganic fillers covered by hydrophobic additives or contaminants. When the enzymatic hydrolysis of ester bond could be made on the surface of hydrophobic particulates, unwanted float of fine particles could be prevented. Now the enhancement of flotation selectivity or the modification of the hydrophobicity of deinking stock is expected to be promoted by the enzymatic pre treatment. And the reduction of recycling cost with the saves of raw material, recovered paper would be possible as a result.

INTRODUCTION

In order to confirm the continuant, sustainable development of paper industry and to promote the production of paper and paperboard in the future, sufficient supply of raw material, in particular recovered paper with keeping up of its quality is inevitably required. Every year newsprint mills of ROK import more than 600 thousands ton of old newspaper from abroad due to the deficiency of supply[1)]. Increase of collecting ratio could be suggested as a solution for the shortage of recovered paper but the recovery ratio of paper and paperboard in ROK is already very high[2)] and so it seems to be no more margin is left for that. Therefore making endeavor to improve the recycling yield becomes very important.

Recycling yield of recovered paper is usually influenced by two major factors, the amount of contaminants and the segregation efficiency of them through the stock preparation stages. Among the various recovered paper, printed one for example, old newspaper shows relatively low recycling yield in particular compared with packaging grade because of loss in deinking process.

Deinking process could be classified into washing and flotation and these days selective segregation of ink by flotation is preferred owing to the less contamination and consumption of process water. The mechanism of ink separation by froth flotation is based on the hydophobicity of contaminant particles.

Ink particles characterized by hydrophobic surface show a strong tendency to adhere to air bubbles and after stick on to the floating air bubble, they are to be segregated from hydrophilic suspended solids for example, hydrated cellulose fibers, fines and inorganic fillers. As it could be expected, the efficiency of flotation deinking process depends upon the surface physico-chemical properties and the hydraulic movement of suspended solids in flotation cell. If the hydrophobic ink particles are completely detached from hydrophilic fiber surfaces, physico-chemical condition for the segregation of ink could be fulfilled for the moment. When the detached ink particles could have an enough chance to collide with air bubbles in flotation cell and when the detached ink particles could be trapped and floated up to the surface by air bubbles, the efficient ink removal could be made.

The amount of ink in deinking stock is below 2% in terms of weight. However the ratio of deinking rejects or loss of pre flotation in ONP recycling process is higher than 10% usually. It means except for the hydrophobic ink particles, pulp fines and inorganic fines are also floated and discharged by air bubbles. Although the pulp fines and dispersed inorganic pigment or fillers have hydrophilic surfaces at first as virgin raw materials, when they are introduced to hydropulper as recovered paper, their surfaces show hydrophobic characteristics by the adsorption of hydrophobic materials including sticky contaminants or wet end chemicals intentionally added before. Here the stickies means various polymeric contaminants including styrene-butadiene rubber (SBR), polyvinyl acetate (PVAc), vinyl acetate (VA), polystyrene (PS), polyisoprene, hot melts (EVA, polyethylene, waxes) and wet end chemicals include sizing agents (AKD, ASA, rosin) which could be characterized by hydrophobicity. Sizing agent added during the papermaking process adsorbed mainly on fines due to the big specific surface area and these fines could be floated easily in deinking cell because of its proper size and surface hydrophobicity. Fragmented stickies also could stick on to the surface of suspended solid and the adsorption of stickies on fine materials could be easier than those on fibers or big particles due to the big specific surface area of fine materials[3]. As a result of previously mentioned phenomena, fine materials including fine cellulosic fiber and inorganic fillers show floating tendency and so the froth-flotation loss is to be aggravated. Here the flotation loss means not only simple lost of raw materials but also waste of energy for stock preparation including pulping, cleaning and coarse screening. The loss of flotation means also unnecessary contamination of process water. As the flotation loss could generate solid waste and water contamination, the endeavor to optimize the flotation efficiency and to reduce the flotation loss is urgently required now. And if we can control the flotation selectivity by modifying the hydophobicity of fine materials in deinking stock, reduction of production cost and saves of recovered paper could be made with the preservation of environment.

DEINKING pH, ALKALINE VERSUS NEUTRAL

Actually modification of the hydrophobic fine materials in deinking stock into hydrophilic one could be done easily by the increase of alkali chemical in pulping stage. Increase of caustic soda can cause the change of the surface chemical properties of suspended solids from hydrophobic to hydrophilic according to the alkaline hydrolysis reaction. That is, when the sufficient amounts of alkali is added to pulping stage, hydration of hydrophobic suspended solids is promoted and so the reduction of flotation rejects is a matter of course. However the increase of alkali dosage in pulping and deinking flotation process may cause the indiscriminative attack of inorganic chemical, base and the excessive dissolving or the fragmentation of contaminants like inks and stickies are unavoidable. Therefore, a special method for the selective modification of valuable hydrophobic particles is required now.

For the control of above mentioned troubles caused by excessive addition of alkali there is a strong tendency of reducing alkali in deinking process of ONP now. Currently suggested neutral deinking of ONP has the primary benefits of significantly reduced chemical costs due to the elimination of caustic, peroxide, chelant, biocide/catalase control, and all or part of the sodium silicate from the pulper. There are other related advantages as well, since several of these eliminated chemicals have serious safety and environmental implications[4]. As above mentioned the driver for neutral deinking is primarily a reduction in chemical costs, which can be significant, although environmental benefits are minimal. However one of the original purposes behind the development of neutral deinking technology was to reduce the number of stickies caused by alkali-soluble latices and adhesives that are readily dispersed when wastepaper is pulped with high alkali levels[5].

Although cleaner and cheaper deinking of ONP could be made at the neutral or low alkaline condition, excessive loss from flotation is unavoidable and so neutral or low alkaline deinking by the reduction of alkali or caustic soda dosage could be regarded as uneconomic. Now the trade-off regarding alkali dosage versus flotation yield should be set for the optimization of neutral or low alkaline deinking efficiency[6,7].

The concern of this study is how to overcome this contradictory relation getting the best of both that is, clean and high yield deinking by new technology, application of bio catalyst enzyme. The use of enzymes could be an attractive alternative to chemicals in deinking: enzymes could improve the de-inkability of inks difficult to detach with the conventional deinking process and since enzymes are used in neutral conditions, they could be supposed to produce a lower COD concentration than conventional alkaline deinking.

In recent years, the application of enzymes in deinking has been studied on laboratory and pilot plant scale. This work has resulted in numerous patents.

Generally there are three different approaches available for the use of enzymes in deinking:

- the fiber surface can be attacked by enzymes
- the starch-based coating can be solubilised by enzymes
- vegetable oil-based binders of the printing inks can be hydrolyzed.

Lipases can be used to hydrolyze soy-based ink carriers and carbohydrate hydrolyzing enzymes, such as cellulases, xylanases or pectinases can be used to release ink from fiber surfaces. Most applications proposed relate to the use of cellulases and hemicellulases. In this case the detachment of ink results from a partial enzymatic hydrolysis of carbohydrate molecules on the fiber surface.

However, so far enzymatic deinking is rarely applied in commercial use and furthermore there is no report regarding the use of enzyme for the improvement of deinking yield[8].

LIPASE FOR DESIZING, DEACETYLATION

Instead of inorganic base, biochemical catalyst called lipase could be applied for the selective surface modification of valuable hydrophobic particles in deinking stock, for example cellulose fines and inorganic fillers covered by hydrophobic materials. Lipase is an enzyme that catalyzes the breakdown of fats into fatty acids and glycerol. If the lipase could cut the ester bond of chemically reacted internal sizing agents, for example AKD and ASA, lipase could be a good solution for the unwanted float of suspended solid.

Among the many kinds of lipases, typical lipase for the control of wood pitch trouble has been used in the manufacturing process of high yield pulp. As this lipase was developed to decompose the wood resin, also the acid sizing agent called rosin-alum could be treated by it.

Fine particles in flotation stock could be covered by adsorbed hydrophobic micro-stickies for example PVAc. If the enzymatic hydrolysis of ester bond (deacetylation) could be made on the surface of PVAc, unwanted float of fine particles would be prevented.

In order to search the possibility of lipase applied desizing or deacetylation reaction, three kinds of commercial lipase were tried in this study. They were lipase called Resinase A2X®, Lipex® and Optimyze® (lipase1, lipase2 and cutinase respectively from now on) supplied by Novozymes.

For the verification of desizing effect of lipase, AKD reacted filter paper was prepared as follows; At first, AKD wax was dissolved in dichloromethane (DCM) at the consistency of 10%. After the preparation of AKD solution, filter paper (Whatman No. 2) was soaked in it for 1min. After air drying, the filter paper was cured at the temperature of 105℃ for 1 hour. Cured filter paper was washed with DCM in order to remove the excessive AKD which could not reacted with cellulose fiber. AKD sized filter paper was soaked in three kinds of 0.1% lipase solutions for 30 min at the temp. of 45℃ with agitation by magnetic stirrer. Lipase treated filter papers were rinsed and dried in the air for the analysis of hydrophobicity of its surface. Dynamic contact angle of water drop was measured before and after the lipase treatment and the results were shown in Fig. 1 & 2.

Contact angle of water drop on AKD sized filter paper before and after soaking in water maintained more than 120°. However lipase 1 and 2 decreased the contact angle of filter papers as much as 50° according to the 30 min soaking. It means reacted AKD could be removed by enzymatic hydrolysis as illustrated in Fig. 3 and based on this result the possibility of lipase applied surface modification could be expected.

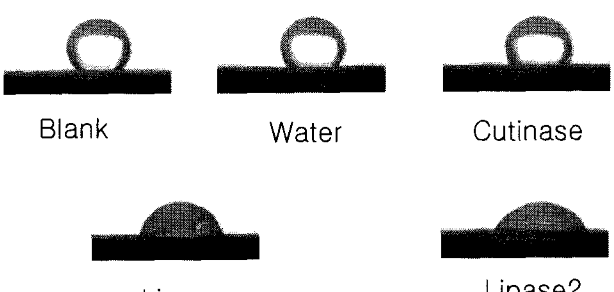

Fig. 1. Contact angle of water drop on AKD sized filter paper before and after lipase treatment.

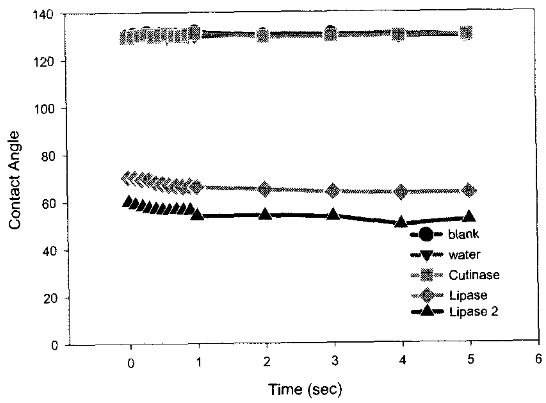

Fig. 2. Dynamic contact angle of water drop on AKD sized filter paper before and after soaking in varied lipase solution.

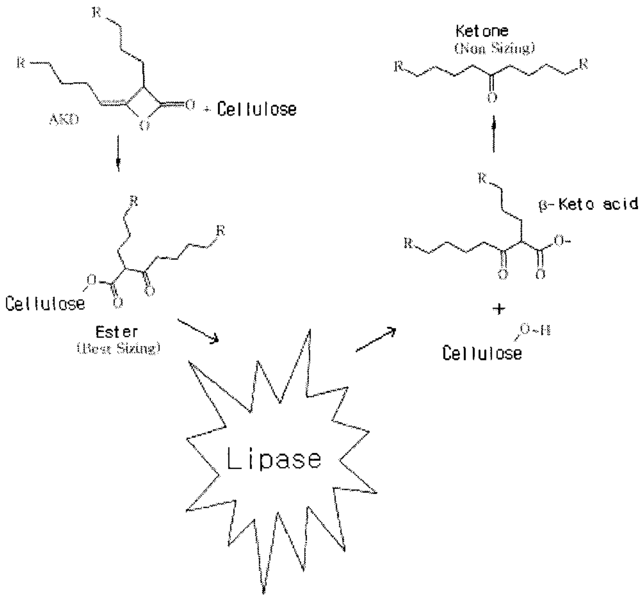

Fig. 3. Lipase applied desizing mechanism of AKD.

ASA sized filter paper was prepared by following vapor sizing procedure. First of all filter papers (Whatman No.2) were put in the chamber saturated with vaporized ASA at the temp. of 105℃ for 3 hours[9]. ASA sized filter papers were soaked in three kinds of 0.1% enzyme solutions for 30 min at the temp. of 45 ℃ with stirring. Lipase treated papers were rinsed and dried in the air in order to measure the water drop contact angle.

As shown in Fig. 4, lipase 1 and 2 changed the hydrophobic surface of the filter paper into hydrophilic one. Similar to the case of AKD, cutinase did not give any significant effect on the decrease of the contact angle of water drop on the ASA sized paper. Cutinase has been used as a stickies control agent and showed good efficiency for the surface modification of micro stickies[10]. However, the activity (protein content) of cutinase is too low compared with the other lipase and so the efficiency of desizing was believed to be insignificant.

Desizing mechanism of ASA by lipase could be suggested as Fig.5.

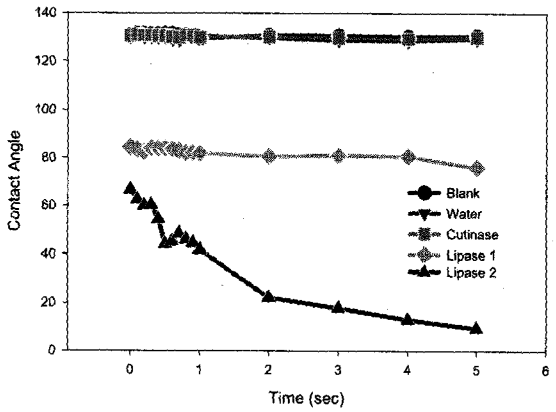

Fig. 4. Dynamic contact angle of water drop on ASA sized filter paper before and after soaking in varied lipase solutions.

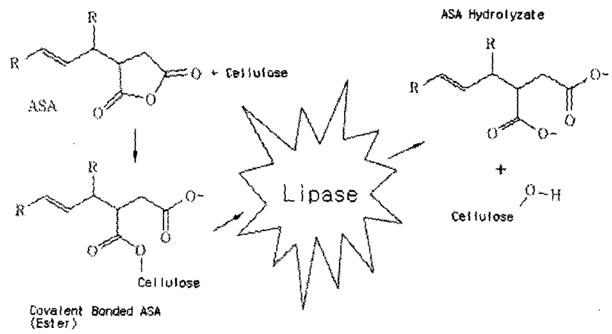

Fig. 5. Desizing of reacted ASA by lipase.

Different from reactive sizing agents AKD or ASA, Rosin dose not form the chemical bond with cellulose. Instead of covalent bonding, rosin reacts with alum and cause the aluminum resinate as a cationic complex which usually sticks onto the hydrophilic surfaces. With a view to verify the desizing effect of lipase, highly rosin sized wall paper broke was disintegrated at the consistency of 2% for 5min using TAPPI Standard disintegrator with (0.1 % based on OD weight of stock) and without lipase 1. Slurry of wall paper broke was beaten by Valley beater for 15min and sampled from beater at 5, 10 and 15min in order to make the pad of 100g/m^2. Water drop contact angle of pad was measured and reported as Fig. 6.

Even after disintegrating and beating, slurry of wall paper broke kept the hydrophobicity. Paper from rosin sized broke recovered hydrophilic surface by the application of lipase and prolonged beating time. Lipase showed good efficiency in desizing of rosin alum added paper. Based on the above mentioned investigation of desizing effect of three major size agent could be confirmed and so surface modification of hydrophobic materials in deinking stock could be anticipated.

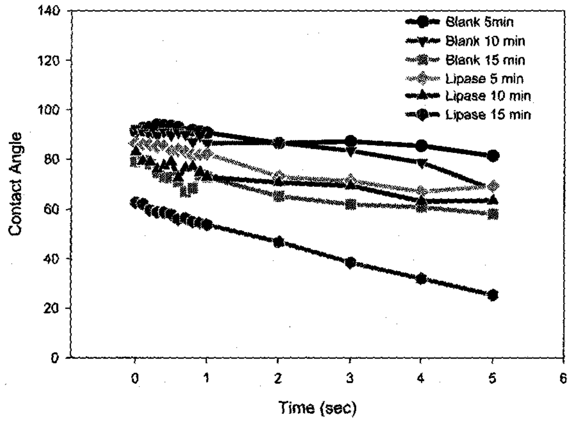

Fig. 6. Water drop contact angle of paper molds from rosin sized wall paper slurry with or without lipase at the varied disintegration time.

Besides size agent, adsorbed micro stickies also can cover the surface of fine materials and hydrophobic fine materials are destined to be floated as reject. In order to search the possibility of lipase applied deacetylation reaction of PVAc, PVAc coated plastic film was prepared first. After homo-polymerization of vinyl acetate(Vinyl acetate monomer was solved in isopropyl alcohol solvent at the consistency of 20%. As a initiator 0.3% AIBN (Azobis isobutyro nitrile, $(CH_3)_2C(CN)N{=}NC(CH_3)_2CN$) based on monomer weight was added and the temperature was maintained at 50℃ for the polymerization. Polymerized PAVc has Mn, Mw and MWD as 4430, 5710 and 1.289 respectively), plastic film was coated with PVAc and the coated films were soaked in three kinds of 0.1% enzyme solutions for 30 min at the temp. of 45℃ with stirring. Soaked films were rinsed and dried in the air in order to measure the water drop contact angle.

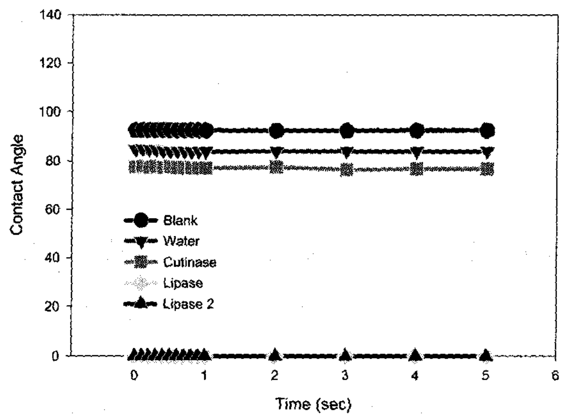

Fig. 7. Dynamic water drop contact angle of PVAc coated plastic film according to the varied lipase treatment.

Effect of enzymatic hydrolysis on PVAc could be confirmed by the result illustrated in Fig. 7. And the lipase reaction against PVAc is supposed to change the surface of deinking stock from hydrophobic into hydrophilic through the mechanism of Fig. 8. Although lipase2 showed better efficiency compared with lipase1, lipase1 was chosen as a proper enzyme for flotation trial according to the consideration of enzyme price.

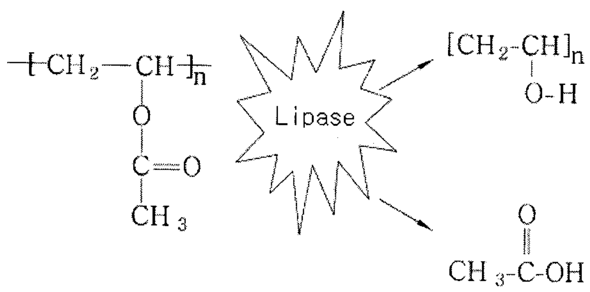

Fig. 8. Lipase applied deacetylation of PVAc.

LIPASE FOR REJECT REDUCTION

The lipase applied modification of hydrophobic materials, chemically reacted or adsorbed on the surfaces of suspended solid particles in deinking stock, seemed to be effective for reducing of flotation reject. In order to verify the above mentioned advantage, froth flotation tests were performed as shown in Fig. 9. As a raw material AKD sized newspaper stock was prepared as follows. Pre Flotation primary stage inlet stock (O.D. 188g) from ONP mill and unprinted newspaper slurry (O.D. 536g) were mixed with and without AKD (1.5% based on OD weight of pulp) + PAE (Polyamide Polyamine Epichlorohydrin, 1%). Dewater and dry the two stocks in dry oven at the temp. of 105℃ for the reaction of AKD size. Reslush the stocks at the low consistency (4%) for 20min using low consistency pulper. After dilute the stock to 1% consistency (230g), perform the lab scale flotation for 4 min after stirring for 15 min in Delta Cell with and without lipase (0.05% based on OD weight of pulp).

As shown in Fig. 10 and 11, lipase gave a significant effect on the increase of accept weight from flotation of AKD sized stock without any change of ERIC value. In case of unsized stock (blank), lipase addition may not cause any difference in terms of accept weight and ERIC value either. It means hydrophobic stock could be changed into more hydrophilic one by the action of lipase. In case of hydrophilic stock (blank), there is no more lipophilic surface to be modified by lipase and so lipase may not give any effect on the yield of the flotation. Although flotation reject was decreased by lipase action, Fig. 12 shows the similar ink removal tendency (the amount of removed ink is equal to the value of flotation reject weight multiplied by ERIC) versus flotation time. Base on the previous result, reduction of flotation reject without any harmful effect on the optical properties of flotation accepts by lipase application could be regarded as possible.

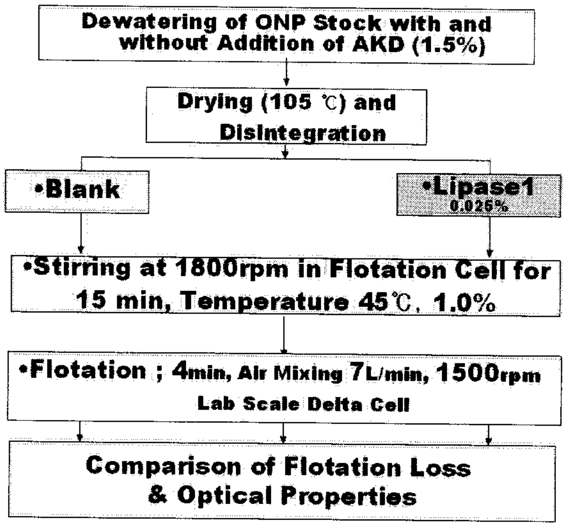

Fig. 9. Block diagram for froth flotation of AKD sized ONP with and without lipase.

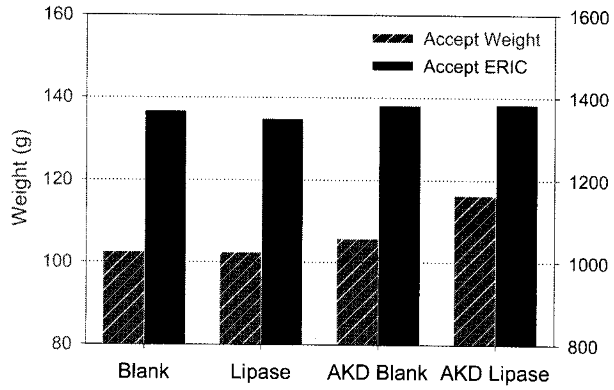

Fig. 10. ERIC and weight of flotation accept according to the size treatment and lipase addition.

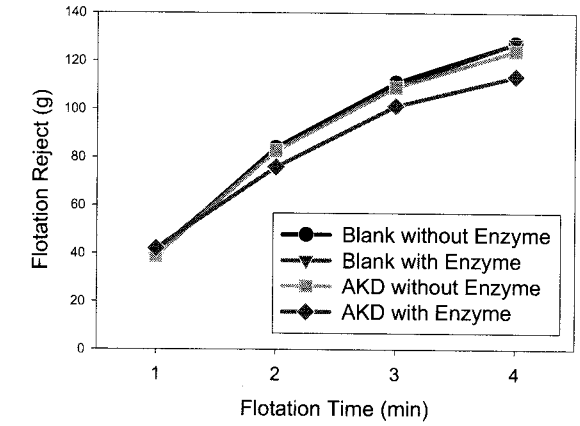

Fig. 11. Flotation reject versus flotation time according to the size treatment and lipase addition.

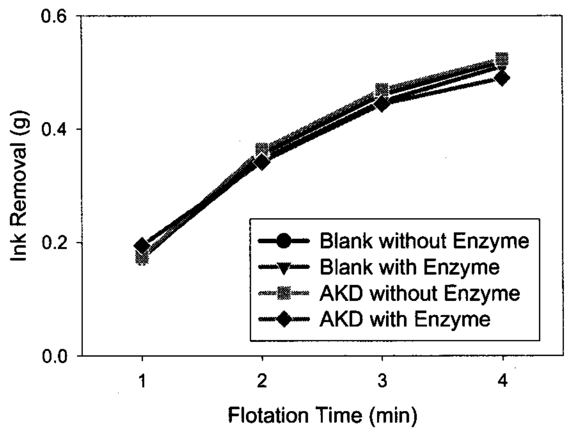

Fig. 12. Ink removal versus flotation time with and without AKD treatment and lipase application.

PRE FLOTATION SECONDARY STAGE

Fig. 13 illustrates the pre flotation process with the scheme of lipase applied secondary froth flotation. In order to test the lipase added secondary flotation, the actual reject from primary flotation was sampled at N mill in JeonJu Korea and 0.025% of lipase was introduced for the 15min reaction in lab scale flotation cell. After agitation flotation was performed for the deinking. Flotation accepts and rejects were analyzed for the evaluation of lipase in terms of reject reduction and ink removal.

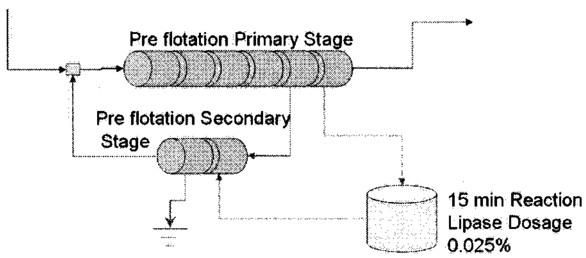

Fig. 13. Flotation process of ONP and scheme of lipase application

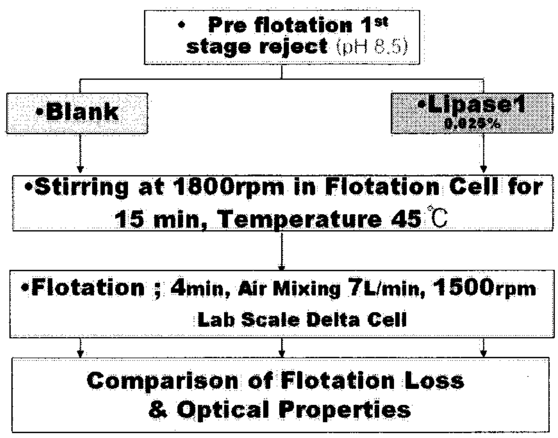

Fig. 14. Block diagram for froth flotation of primary reject of ONP with and without lipase.

Whole of the test procedure was shown in Fig. 14 as a block diagram.

Fig. 15 shows that the accept weight of lipase added case was bigger than that of blank as much as 19.1% at the reject ratio of 45%. Generally ERIC of flotation accepts should be sacrificed for the increase of flotation yield. However the ERIC of accepts from lipase introduced flotation was not increased as shown in Fig. 15.

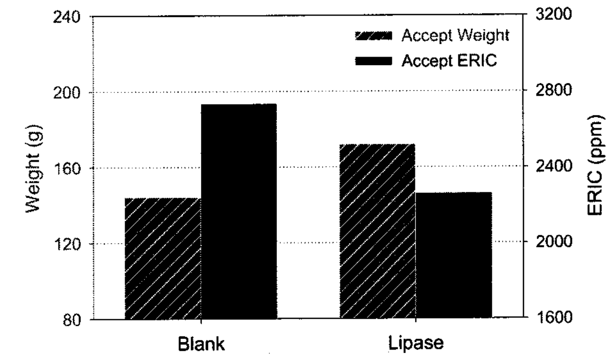

Fig. 15. Accept weight and its ERIC of primary reject flotation with and without lipase

Proportional to the increase of flotation accept, the amount of reject was reduced as much as 16% at the reject ratio of 45% (Fig. 16).

Fig. 17 informs the ash content of flotation reject did not show any difference between blank and lipase added cases. Flotation rejects are containing more than 70% of ash and the rest of rejects is fine organic particles including cellulosic particles. Based on the result shown in Fig. 17 it could be confirmed that the inorganic pigment and organic fines are saved at the same ratio of their composition when the flotation rejects are reduced by lipase application.

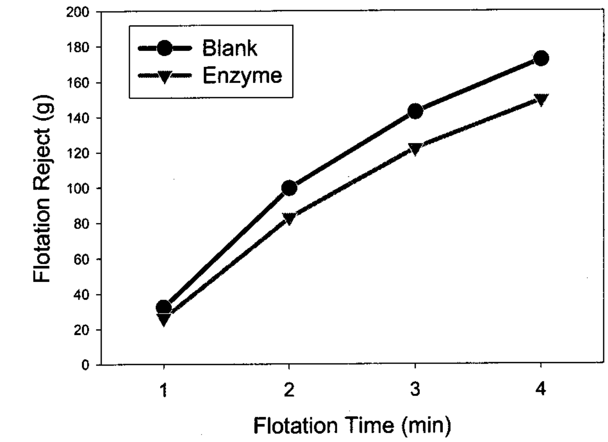

Fig. 16. Reject weight of primary reject flotation according to the operation time.

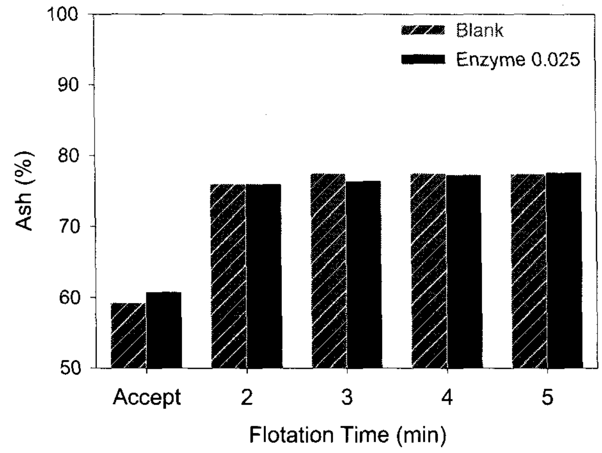

Fig. 17. Ash contents of reject from primary reject flotation with and without lipase.

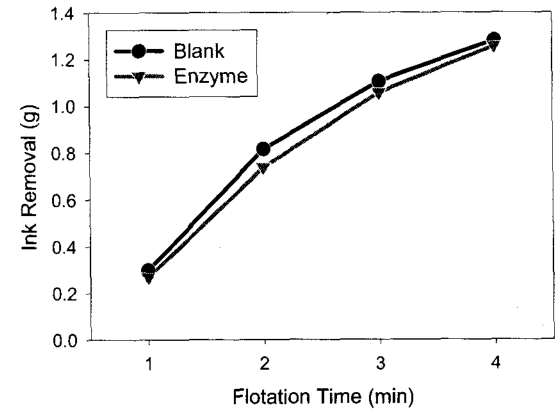

Fig. 20. Ink removal of primary reject flotation with and without lipase.

Fig. 18 and 19 show the ERIC and brightness of flotation reject. Lipase applied flotation discharged darker reject due to the less inclusion of fines at the same removal amount of ink (Fig. 20).

Fig. 21 shows about 22% of flotation reject could be reduced by the lipase application at the same ink removal condition.

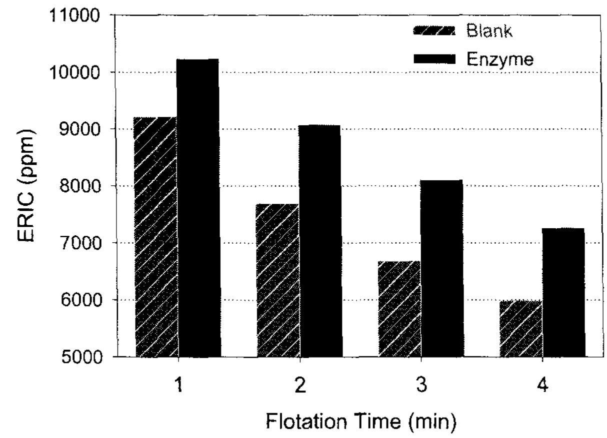

Fig. 18. ERIC of reject at the varied flotation time with and without lipase application.

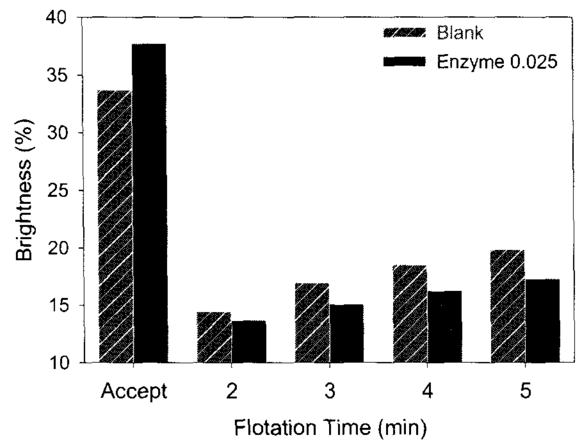

Fig. 19. Brightness of reject at the varied flotation time with and without lipase application.

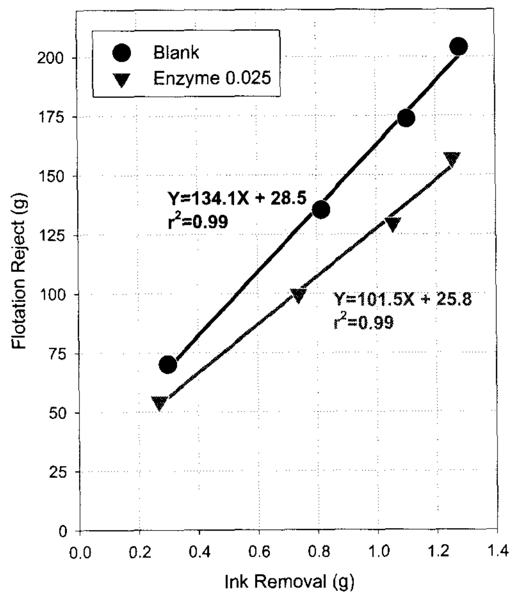

Fig. 21. Ink removal versus the amount of flotation reject.

CONCLUSIONS

Lipase from *Thermomyces Lanuginosus* showed desizing and deacetylation effects and it could be applied to the pre flotation secondary stage in order to reduce the reject without the sacrifice of optical properties of final products.

As we can control the flotation selectivity by modifying the hydrophobicity of fine materials in deinking stock through enzymatic pre treatment, reduction of production cost and saves of recovered paper could be pursued with the preservation of environment.

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