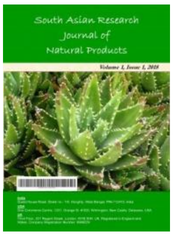

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Green Chemistry of Micro-and Nanoparticles of Plant Biomass

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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ABSTRACT

Some green technologies of biomass processing such as the production of micro-size composites of biomass, microcrystalline and nanocrystalline cellulose have been explored in this study. Sizes of particles, crystallinity and degree of polymerization of cellulose, as well as yield of micro- and nanoproducts and their production cost were studied. Basic principles of green chemistry were implemented using plant biomass as a renewable natural-based raw material. Liquid and solid production wastes were converted into valuable by-products, the sale of which can cover part of production expenses of primary products. Furthermore, used water was recycled and returned to the production line. As a result, various micro- and nanoproducts were obtained from plant biomass without discharge of production waste into the environment. It has also been shown that the production cost of micro- and nanoproducts can be reduced to a great extent.

Keywords: Micro-size composites of biomass; microcrystalline cellulose; nanocrystalline cellulose; zero waste discharge; green chemical technology.

1. INTRODUCTION

As is known, plant biomass includes various plant-based materials such as terrestrial plants (e.g. wood, herbs, agricultural plants, etc.) and plant polymers (cellulose, hemicelluloses, lignin, etc.), as well as residues and wastes of plant materials [1]. Moreover, huge amounts of aquatic

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plants also can be used as appropriate feedstock for biomass processing. The plant biomass is inexpensive, abundant and renewable natural material, resources of which increase by 100 billion tons annually as a result of the photosynthesis reaching 1.5 trillion tons [2,3].

Although biomass is a renewable and biodegradable source, chemical technologies of its processing are accompanied by a large amount of gaseous, liquid and solid waste polluting the environment. For example, the production of 1 ton of pulp and paper generates 40-60% organic waste and 10-20 m^3 of wastewater [4,5]. It is also known that annually about 200 mil. tons of the waste paper and board are thrown away, landfilled or incinerated. To reduce the number of biomass wastes a technology was proposed to convert the biomass into levulinic acid, which however is far from being environmentally friendly [6,7].

Other paths for utilization of the biomass are the production of widely used micro-sized biomass composite, microcrystalline cellulose and nanocrystalline cellulose [8,9]. However, current technologies of these products are harmful and cause the environmental pollution.

To turn a chemical processing really into "green", it is necessary to implement the basic principles of green chemistry formulated by Anastas and Warner [10]. Along with these principles, there are also some other ideas related specifically to the green chemistry of biomass to produce micro- or nanoproducts. In order to reduce production expenses, the product must be manufactured directly at a pulp mill using its infrastructure, energy, water and inexpensive pulp as a feedstock. Liquid and solid production wastes should be used as raw materials for manufacturing of valuable by-product, the sale of which can cover part of production expenses of the primary product. It should be provided the complete recycling of used water and its return to the production line. Optimal production conditions should be found to increase the yield, prevent feedstock losses and reduce the consumption of chemicals and energy. Extremely costly and low-productive process of fine comminuting should be avoided. Also, the drying process should be avoided because it requires increased energy consumption.

The main purpose of this research was the development of some green chemical technologies for the production of micro-size biomass composite, microcrystalline and nanocrystalline cellulose at a low cost without discharge of production waste into the environment. General schemes of green technologies have been proposed and experimentally tested. Chemical composition and some other characteristics of raw materials were analyzed. Samples of micro- and nanoproducts were obtained and their characteristics were studied. Besides, the cost of these products was also evaluated.

2. MATERIALS AND METHODS

2.1 Materials

Various paper and board wastes (PBW) were chosen as raw-materials, such as used newspaper (NP), wrapping paper (WP), office and printing paper (OP), tissues and napkins (TN), corrugated (CB), egg carton (EC), which were supplied by Amnir Recycling Ind. (Israel).

Bleached Kraft pulp (92% α-cellulose, DP=1100) was supplied from Weyerhaeuser (USA). Besides some chemicals were used such as pure 95% sulfuric acid, sodium carbonate, calcium carbonate, calcium oxide and technical hydroxylapatite.

2.2 Method for Production of Composites Containing Microparticles of Paper/Board and Inorganic Substances

Wastes of paper and/or board were cut into 1-3 cm pieces and put into a reactor. Then, 15 wt. % sulfuric acid (SA) was slowly added to feedstock while stirring to obtain liquid/solid ratio (LSR) of 5 to 10. The reactor was heated to 100°C and maintained at this temperature for 1 h while stirring. The reactor was cooled to room temperature, and the required amount of calcium carbonate or oxide was added to acidic slurry of microparticles to neutralize the acid and obtain gypsum as a by-product, as follows:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2$$

$$H_2SO_4 + CaO \rightarrow CaSO_4 + H_2O$$

After blending, the final product was obtained, namely a composite that consisted of microparticles of paper/board (PB), gypsum and some other inorganic substances containing in the feedstock.

2.3 Method for Production of Microcrystalline Cellulose (MCC)

The feedstock, bleached Kraft pulp, was cut into 1-3 cm pieces that were mixed with water in a blender, and the resulting slurry was filtered using a vacuum filter to final solids content of 40-50 wt. %. Wet pulp was put into a reactor, and then 80 wt. % sulfuric acid was slowly added while stirring to obtain the required acid concentration of 15 wt. % and LSR of about 10. The reactor was heated to 100°C and maintained at this temperature for 1 h while stirring to hydrolyze amorphous domains of cellulose. After acidic treatment the reactor was cooled to room temperature. The obtained MCC slurry was separated from the acid solution by filtration on a vacuum filter and washed to neutral pH value separating the acidic water by filtration. Moreover, all acidic wastewater was collected together and neutralized with powdered hydroxylapatite (HAP) to obtain the superphosphate by-product, as follows:

$$7H_2SO_4 + 2Ca_5(PO_4)_3OH \rightarrow 3Ca(H_2PO_4)_2 \times 7CaSO_4 + 2H_2O$$

2.4 Method for Production of Nanocrystalline Cellulose (NCC)

Pieces of initial Kraft pulp were mixed with water in a blender, and the resulting slurry was filtered using a vacuum filter up to final solids content of 40-50 wt. %. Wet pulp was put into a reactor, and then 80 wt. % sulfuric acid was slowly added while stirring and cooling to obtain the required acid concentration of 60 wt. % and LSR of about 10. The reactor was heated to 45°C and maintained at this temperature for 1 h while stirring to hydrolyze the amorphous domains of cellulose. After acidic treatment double volume of water was added into reactor while stirring to stop the hydrolysis process. The sediment of hydrolyzed cellulose was separated from the acid solution by centrifugation and additionally washed three times separating the acidic water by centrifugation. The washed sediment containing low amount of residual acid was complete neutralized with 1% sodium carbonate, additionally washed and centrifuged to obtain cellulose nano-product, i.e. wetcake of NCC. Besides, all acidic wastewater was collected together and neutralized with powdered HAP to obtain the superphosphate by-product.

2.5 Methods of Analysis

The chemical composition of initial feedstocks and obtained products was studied by standard methods of chemical analysis [1,11]. The degree of crystallinity of the cellulose samples was determined by method of wide angle X-ray scattering [12]. Size and shape of particles were investigated by method of electron microscopy [13]. The average degree of polymerization, DP, was measured by the viscosity method using diluted solutions of cellulose in Cadoxen [14].

3. RESULTS AND DISCUSSION

3.1 Green Chemical Technology of Composites Containing Micro-particles of Paper/Board and Inorganic Substances

For this purpose, various paper and board wastes (PBW) were used as raw-materials. The studied composition of these raw-materials is shown in Table 1.

Currently global paper and board production is estimated in 410 mil. tons per year. Share of cardboard production is about 45% and paper about 55% including 10% of newspaper, 17% of tissues and napkins, and 27% of office and printing paper. After usage about 50% of PBW are recycled, whereas about 200 mil. tons of the wastes are thrown out, landfilled or incinerated. Such a huge amount of PBW can be used as cheap feedstock to produce a composite containing microparticles of paper/ board (PB), gypsum and some other inorganic

Table 1. Chemical composition of paper and board wastes in %

PBW	Cellulose	*Hemi	Lignin	**INOS	Others
CB	81	8	6	3	2
EC	68	11	12	7	2
NP	55	17	21	5	2
WP	60	11	7	21	1
TN	58	6	4	29	3
OP	64	5	0	30	1

**Hemi denotes hemicelluloses; INOS denotes inorganic substances*

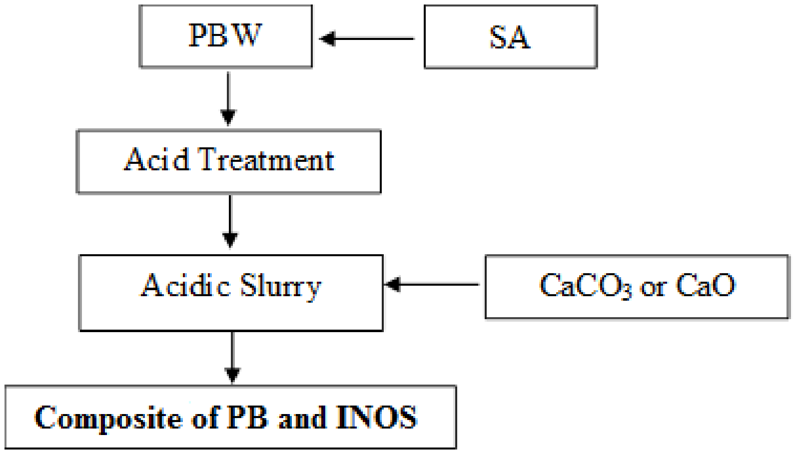

Fig. 1. General scheme of production process of composite containing microparticles of paper/board and INOS

substances using a novel green technology. The general production scheme is shown in Fig. 1. (Shown above)

For example, feedstock is a mixed waste of CB and EC that contains 85-90% ligno-carbohydrates and 4-5% inorganic filler, mainly kaolin. Other example, feedstock is a mixed waste of NP, WP and TN containing 75-80% ligno-carbohydrates and 17-19% inorganic filler. After acidic treatment of this feedstock at LSR=5 and subsequent neutralization of the acid with calcium oxide (see method 2.2.), a light-brown paste was formed. This paste contained 13-15% PB, 1-2% oligosaccharides, 20-25% INOS and 60-62% water. The obtained paste can be used for coating of drywalls and production of gypsum or gypsum-cement putties.

Third example: feedstock is a waste of OP that composes 64% cellulose and 30% inorganic filler - calcium carbonate. In this case, after acidic treatment of this feedstock at LSR=10 and subsequent neutralization of the acid with calcium oxide, a white paste containing 5-6% cellulose particles (CP), 18-19% gypsum and 75-76% water was obtained. This paste can find application as a filler or opacifier for various coating compositions, e.g. for production of liquid wallpaper.

Structural studies have shown that obtained composites contain rod-like microparticles of biomass with sizes of 50-200 x 20-40 µm, along with round microparticles of gypsum and some other inorganic substances with diameter of 5-20 µm (Fig. 2).

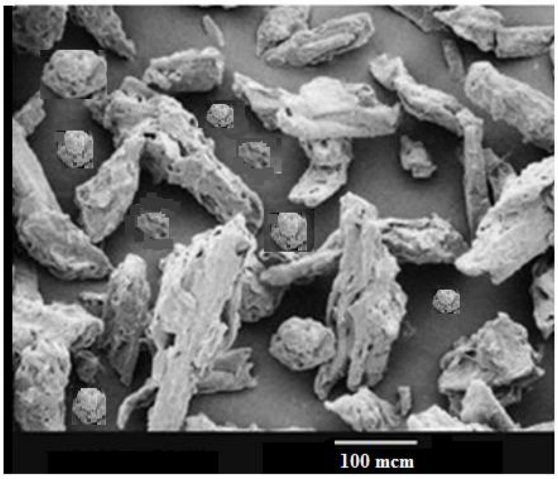

Fig. 2. SEM image of composite containing aggregates of rod-like microparticles of biomass and round microparticles of INOS

As a result of economic calculations, the production cost of PB-INEOS and CP-INEOS composites was evaluated at $40 per ton (see appendix, Tables 2 and 3). The proposed green technology provides the complete utilization of feedstock, chemicals and water. Furthermore, the used acid is converted into valuable by-product such as gypsum. The cheap paste is obtained with zero-discharge of production waste into the environment.

3.2 Green Chemical Technology of Microcrystalline Cellulose

As is known, microcrystalline cellulose (MCC) is widely used as an inactive ingredient of tablets, cosmetic formulation and food products, as well as filler and special additive for some technical applications [15]. Currently, MCC is produced by depolymerization of cellulose materials with solutions of dilute (1-3 N) mineral acids at increased temperatures up to level-off degree of polymerization (LODP), which approximately corresponds to average length of individual nano-crystallites of cellulose [16]. After cellulose hydrolysis, MCC is separated from the acid, washed, dried and grinded. Another technology is that washed MCC is diluted to 1-3% and then spray dried to obtain beads of MCC [17]. Acidic wastewater is neutralized and discharged to sewage system. Both existing MCC-technologies pollute the environment; moreover, the production cost of solid MCC is high and reaches $8000 per ton [18].

To overcome the shortcomings of existing methods, a green technology for MCC production has been developed, scheme of which is shown in Fig. 3.

The feedstock can be, for example, bleached Kraft pulp supplied directly from the pulp mill at a reduced cost of about $350 per ton. The initial pulp was treated with 15 wt. % SA in accordance with method 2.3. As a result, about 40% wetcake of MCC was obtained along with by-product such as superphosphate. Neutral wastewater was returned in the production line to use for wetting of pulp, preparation of solutions and washing of hydrolyzed cellulose.

Structural studies showed that MCC wetcake contains particles with sizes of 50-150 x 20-30 µm (Fig. 4). Crystallinity degree of MCC was 71-73% and DP was 150-170.

As a result of economic calculations, the production cost of 40% MCC wetcake was evaluated at $186 per ton wetcake, i.e. $465 per ton of solids MCC (see appendix, Table 4).

The proposed green technology provides the complete utilization of acidic wastewater for production of valuable by-product such as superphosphate fertilizer, the sale of which covers part of the MCC production cost. The MCC was obtained without discharge of production waste into the environment. Besides, washing water was returned to the production line. As a result, production cost of MCC is relatively low. This product can be used as modifying agent in personal care remedies, cosmetics, pharmaceutics and some other areas.

3.3 Green Chemical Technology of Nanocrystalline Cellulose

Nanocrystalline cellulose (NCC) is characterized by increased crystallinity, developed specific surface, biodegradability, stability to aggressive medium, increased temperatures and proteolytic enzymes, etc. Due to these features, NCC has diverse potential application as reinforcing additive for papermaking, high-quality filler for polymer composites, glues and coatings, nano-carrier of biologically and therapeutically active substances, etc. [19-24].

Typical methods for preparation of NCC were described in [25-27]. Feedstock - microcrystalline

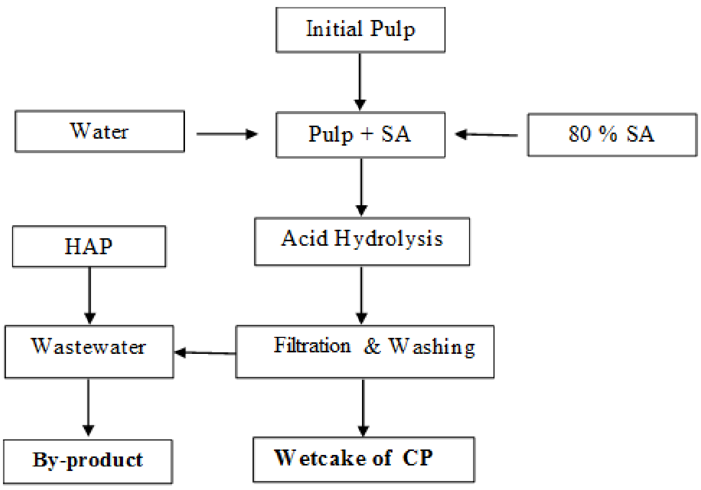

Fig. 3. General scheme of production of wetcake containing cellulose particles (CP)

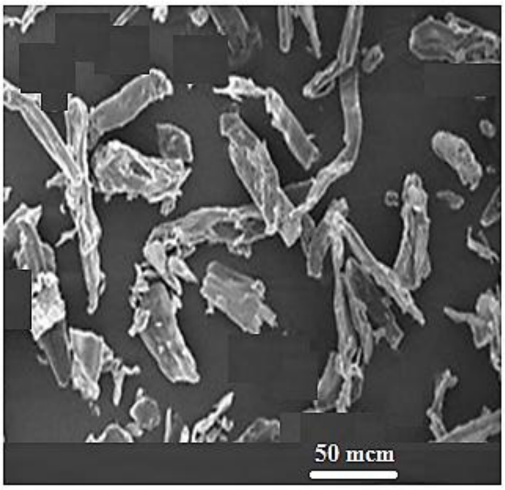

Fig. 4. SEM image of MCC particles

cellulose or other expensive cellulose feedstock, was mixed with deionized water for swelling to accelerate the impregnation process of the cellulose sample by concentrated sulfuric acid (SA) having a high viscosity. The cellulose dispersion in water was placed in a beaker, and concentrated SA was slowly added while stirring and cooling to obtain the desired LSR of about 10 and acid concentration of about 63-65 wt. %. The acidic treatment was carried out at 45°C for 1-2 h while stirring. The cellulose sediment was separated from the acid solution and washed using a centrifugation. The centrifugation step was stopped after five washing cycles at least. The product was dialyzed with deionized water until the wash water maintained at neutral pH. To break up aggregates and isolate individual particles of NCC, the washed product was diluted with water to 1% concentration and sonicated for 30 min.

However, the existing methods for isolation of NCC particles from cellulose are far from optimal. Firstly, these methods are complex, multi-stage, low productive and lead to low yield of the final product. Secondly, these methods are based on the use of expensive feedstock and require a high consumption of chemicals, water and energy. Thirdly, the existing methods are accompanied by formation of huge volumes of acidic wastewater polluting the environment. Fourthly, because of the use of too concentrated SA (63-65 wt. %) final yield of NCC is low, 25-30% only. Fifthly, both dialysis and sonication techniques are not suitable for industrial production. Sixthly, the production cost of NCC is extremely high.

Therefore the purpose of this part of the study was to develop an improved green and cost-save chemical technology for production of nanocrystalline cellulose without polluting the environment. General scheme of the green production process of NCC was the same as for the production of MCC (Fig. 3).

The feedstock was bleached Kraft pulp supplied directly from the pulp mill at a reduced cost of about $350 per ton. The initial pulp was treated with 60 wt. % SA in accordance with method 2.4. As a result, cellulose nano-product, i.e. wetcake of a paste consistency containing of about 25% of NCC, was obtained along with superphosphate as a by-product. Besides, neutral wastewater was returned to the production line.

Structural studies showed that NCC contains rod-like nanocrystalline particles with sizes of 120-150 x 10-15 nm (Fig. 5).

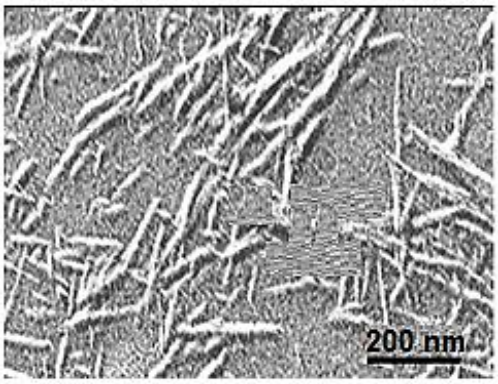

Fig. 5. SEM image of NCC particles

Degree of polymerization of NCC was 120-140 and crystallinity degree of nanocrystalline particles determined by X-ray method was 73-75% (Fig. 6).

Thus, the proposed green technology of NCC provides the complete utilization of acidic wastewater for the production of valuable superphosphate fertilizer, the sale of which covers part of the production cost of NCC in a paste form. The cellulose nano-product was obtained without discharge of production waste into the environment; moreover, washing water was returned to the production line. As a result, production cost of 25% paste of NCC can be reduced to $155 per ton, i.e. to $619 per ton of solids nano-product (see appendix, Table 5). The obtained paste of NCC can be applied as

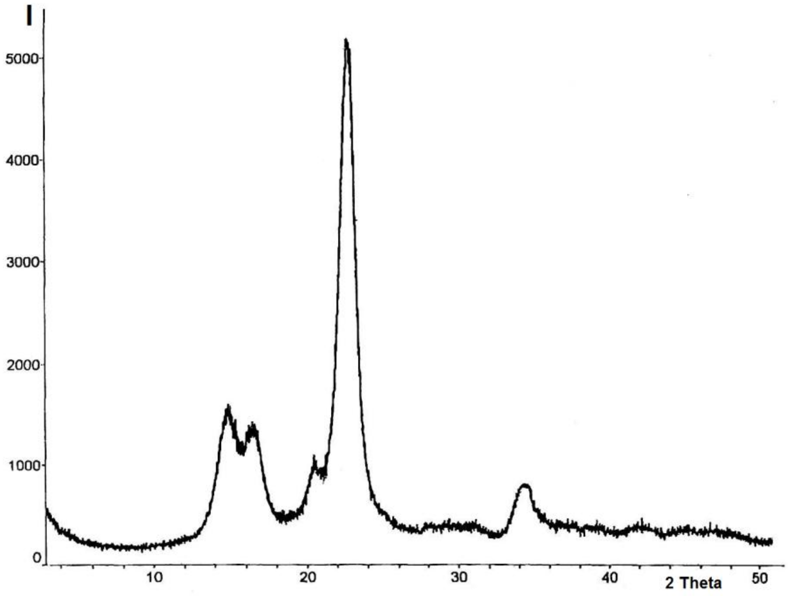

Fig. 6. X-ray diffractogram of NCC particles

modifying additive for composition of papers, glues, coatings, latexes or solutions of polymers, followed by homogenization, casting and drying.

4. CONCLUSION

In this study, some green technologies of biomass processing such as production of micro-size composites, microcrystalline and nanocrystalline cellulose were explored. It was shown that various micro-and nano products can be obtained from plant biomass together with the conversion of liquid and solid production wastes into valuable by-products, the sale of which can cover part of production expenses of primary products. Besides, used water was recycled and returned to the production line. As a result, the production cost of micro- and nanoproducts can be significantly reduced.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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APPENDIX

To calculate the production cost the following parameters were taken into account: price of initial raw-material, cost of chemicals, water and energy using for heating, mixing, centrifugation, filtration, etc. (Tables 2-5).

Table 2. Cost of initial raw-materials, chemicals, water and electric energy

Item	Cost
PCW	$50 per t
Initial pulp	$350 per t
95% H_2SO_4	$95 per t
Na_2CO_3	$150 per t
$CaCO_3$	$50 per t
HAP	$100 per t
Water	$8 per 10 m^3
Electric energy	$100 per MWh

Table 3. Expenses for production of micro-size composite

Item	Amount	Cost, $
Initial PBW	1 ton	50
H_2SO_4	750 kg	75
$CaCO_3$	765 kg	38
Water	5 m^3	4
Energy	0.55 MWh	55
Subtotal:		222
*Overhead (15%):		33
Total expenses:		**255**
Yield of composite	6.43 ton	
Production cost:		**$40 per ton**

Overheads include salary, amortization, tax, etc

Table 4. Production expenses of MCC

Item	Amount	Cost, $
Initial pulp	1 ton	350
H_2SO_4	1.5 ton	150
HAP	2.2 ton	220
*Water	50 m^3	0
Energy	1 MWh	100
Subtotal 1:		820
Overhead (15%):		123
Subtotal 2:		943
Selling of SPh	3.62 ton	-543
Total expenses:		**400**
Yield of solid MCC	0.86 ton	
Production cost:		**$465 per ton**

Since water is returned to production line, its expense is close to zero

Table 5. Production expenses of NCC

Item	Amount	Cost, $
Initial pulp	1 ton	350
H_2SO_4	6 ton	600
HAP	8.78 ton	878
Na_2CO_3	100 kg	15
*Water	50 m^3	0
Energy	1.3 MWh	130
Subtotal 1:		1973
Overhead (15%):		296
Subtotal 2:		2269
Selling of SPh	14.5 ton	-1885
Total expenses:		**384**
Yield of solid NCP	0.62 ton	
Production cost:		**$619 per ton**

**Since water is returned to production line, its expense is close to zero*

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