Denickling of Fatty Acid Pitch

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Unsaturated fatty acids are usually hydrogenated with a nickel catalyst. As a side reaction, nickel dissolves in the fatty acids and forms nickel soaps. On refining the crude fatty acid feedstock by distillation, these nickel soaps are enriched in the bottom fraction (pitch) to a concentration range of 2,500–5,500 ppm. With a heat value comparable to heavy fuel oil, the pitch has been used as fuel. However, due to new environmental restrictions, the nickel concentration must be considerably reduced to limit gas emission of nickel. In this study, solvent extraction was investigated as a separation method for denickling of this valuable oleochemical by-product. At a temperature of 80°C, the nickel content in the pitch was reduced from 2,900 ppm to 4 ppm in three extraction steps by means of 1 wt% citric acid in water. Based on experimental results, a preliminary process flowsheet is presented consisting of extraction, stripping, acid washing and electrolysis. An economic analysis, performed on the extraction process and a process based on direct combustion followed by electrostatic precipitation revealed that direct combustion is economically more advantageous. However, the compatibility of the extraction alternative can be considerably improved by process optimization. The type and concentration of the stripping and acid washing agents, phase ratios, temperature, ionic strength and the equilibrium pH of the aqueous and acid phases are important process parameters that should be considered in the optimization process.

KEY WORDS: Denickling, fatty acids, pitch, solvent extraction.

World production of fats and oils in 1990 has been estimated at 80.6 Mton (million metric tons) and is projected to reach 105 Mton by the year 2000 (1). Palm oil and palm kernel oil are steadily displacing tallow and coconut oil, respectively, due to the rapid increase of mature oil palm areas. According to the same source, world production of natural fatty acids in 1988 was 2.23 Mton and is projected to increase at an average annual rate of 2.1% to reach 2.86 Mton by the year 2000. These figures do not include synthetic fatty acids, originating from petrochemical feedstocks or tall oil fatty acids.

The process for obtaining fatty acids from fats and oils has been described (2,3). Figure 1 displays a simplified block diagram for industrial processing of fatty acids. Individual fatty acids with purities in excess of 99% have been produced by fractional distillation in multicolumn configurations (4–6). On refining the crude fatty acid feedstock by distillation, the nickel soaps are enriched in the bottom fraction, fatty acid pitch, to a concentration range of 2,500–5,500 ppm. With a heat value comparable to heavy fuel oil, the pitch has been used as fuel. However, due to new Swedish environmental restrictions, the nickel concentration first must be reduced to 15 ppm.

Different denickling alternatives. A literature survey revealed that basically there are three different alternatives for denickling of technical-grade fatty acids and/or fatty acid pitch: (i) denickling of both fractions by the dissolution of Ni with hydrogen gas under high pressure followed by hydrogen-pressurized filtration (7); (ii) direct combustion of fatty acid pitch followed by flue gas cleaning in an electrostatic filter (8); (iii) denickling of both fractions by solvent extraction (9).

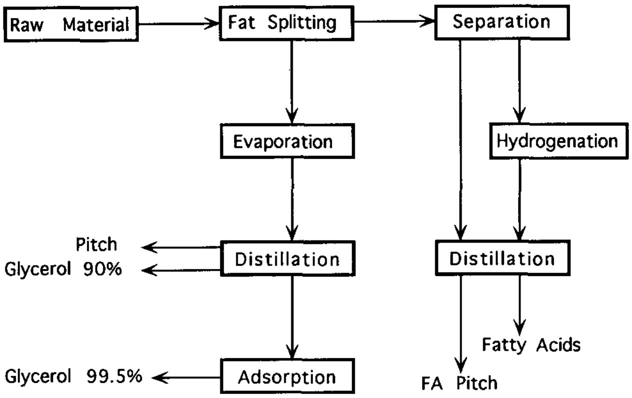

FIG. 1. Block diagram for general processing of fatty acids (FA).

In the first alternative, a number of autoclave experiments were performed on technical-grade oleic acid and stearic acid pitch. The nickel content in oleic acid was reduced from 200 ppm to 5–20 ppm and in the stearic acid pitch from 4200 ppm to 9–29 ppm, depending on different operation conditions. Besides the high pressures and temperatures required, the hold-up time in the autoclave was rather long: 60–230 min. Furthermore, a considerable amount of the fatty acid pitch will be adsorbed on the bleaching earth. Hence, this acid and nickel-laden filter aid has to be disposed of and the resulting disposal costs are difficult to estimate, taking into account future environmental restrictions.

In the second alternative, the nickel content of both the fly ashes and the combustion residual of the boiler will be 35–40%. The ashes can be disposed of, or treated in a recycling plant to recover Ni by means of a magnetic trap or an appropriate hydrometallurgical process. Again, the disposal costs must be considered while taking into account future environmental restrictions. Moreover, large volumes of flue gases must be cleaned down to low concentrations. According to Swedish legislation, the dust concentration in combustion flue gases from fuels rich in heavy metals should not exceed 5 mg/Nm^3, and this limit is expected to be lowered in the near future to 2 mg/Nm^3.

In the third alternative, extraction can be applied on either the pitch or hydrolyzed fatty acid mixtures before distillation. For fatty acid pitch, the nickel concentration should be reduced from 2500–5500 ppm to 15 ppm, whereas this limit would be 1 ppm if extraction is applied to hydrolyzed fatty acid mixtures because the concentration of nickel soaps is amplified about 15 times during distillation. For both cases, the nickel complex formed must be separated from the aqueous phase for subsequent upgrading and recovery. This can be achieved in different ways, such as

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chemical precipitation by salt carbonates or hydrates, zeolite adsorption, or stripping with an organic extractant with a higher selectivity with respect to nickel, and subsequent acid washing and electrolysis.

The main objective of the current study was to investigate both technical and economic feasibility of the extraction alternative, applied on both technical-grade fatty acids and on fatty acid pitch. The results are also compared to the direct combustion alternative. The study has been conducted in close cooperation with a major Swedish producer of technical-grade fatty acids.

EXPERIMENTAL PROCEDURES

To denickel highly viscous liquids, such as C_{10}–C_{22} fatty acids (FA) and their distillation residues (FA pitch), by means of solvent extraction, the process temperature should be ⩾ 65°C. This temperature limit excludes a number of solvents commonly used in metal extraction. Furthermore, aqueous citric acid solutions together with silica-based bleaching earth are currently used in conventional oil refining processes to remove catalyst residues and other metal traces from edible oils. Because of its high affinity to Ni, nontoxicity and relatively low price, citric acid was therefore the only extractant investigated in this study. Both technical-grade C_{16}–C_{18} FA and its pitch were used as feedstocks in the extraction experiments. Process parameters such as citric acid concentration, volume of water phase, type and concentration of adsorbent, temperature, pH and extraction time were investigated to establish their influence on the extent of Ni extraction.

A total of 47 extraction experiments were conducted on C_{16}–C_{18} FA (10). The initial nickel concentration in the FA varied between 361 and 395 ppm. The above process parameters were varied in the range of 0.46–17.5 mol citric acid/mol Ni, 0–12 mL water, bleaching earth, Trisyl and Trisyl 300 as adsorbing agents with concentrations of 1–10 g adsorbent/g citric acid, temperatures of 65–90°C, pH of 1.54–2.30, and times of 0.5–60 min, respectively. Trisyl and Trisyl 300 are developed by W.R. Grace Inc. (South Pittsburgh, TN) to adsorb phospholipids, soaps and metal traces from fatty acids and consist of pure synthetic silica (>99.9 wt%). The citric acid solution was added, with or without the silica adsorbent, to a batch of 50 g FA in a temperature-controlled extraction cell, and the mixture was stirred at 840 rpm for 30 min to attain equilibrium. To enable the separation of FA/FA pitch from the aqueous phase at room temperature, a solvent such as methyl isobutyl ketone (MIBK), xylene or toluene was required. After the extraction, 200 mL of the solvent was added, and the mixture was stirred at the same rpm for one minute. For single-stage extractions, the cell contents were centrifuged to separate the adsorbent, the mixture was allowed to separate into aqueous and organic phases and a small volume (10%) of the organic phase was vacuum evaporated at 85°C for 20 min to strip off the solvent. For multistage extractions, the mixture was first vacuum filtered to separate the adsorbent, followed by phase separation and vacuum evaporation of the fatty phase. The latter procedure was necessary to perform the subsequent treatment steps of extracting, stripping and acid washing. Nickel was analyzed in the solvent-free fatty phase and the aqueous phase on Varian (Palo Alto, CA) SpectrAA 10 and Varian SpectrAA 5 atomic absorption spectrometers, respectively.

The same experimental procedure was applied to the FA pitch, and a total of 27 extraction experiments were performed (10). In this case, all experiments were carried out at the same temperature (80°C), pH (1.95), mixing intensity (840 rpm), extraction time (30 min) and with 20 mL of water. The citric acid concentration was varied in the range of 1.5–169 mol citric acid/mol Ni, and bleaching earth was used as an adsorbent with a concentration of 0–10 g adsorbent/g citric acid. The average initial nickel concentration in the FA pitch was 2,900 ppm.

RESULTS

Figure 2 displays nickel concentration, with Trisyl as adsorbent, as a function of pH with the water volume added as parameter. The pH was calculated before extraction based on the used amounts of citric acid and water. The extraction of FA strongly depends on the mass transfer area. The reduced ability of Trisyl to adsorb Ni at lower and higher pH can be explained by the competition of hydrogen ions with Ni in bonding to the silica surface and by the reduction in citric acid concentration, respectively. Trisyl 300 failed to yield compatible results. Figure 3 shows a comparison between the adsorbing capacity of Trisyl and bleaching earth. The latter agent did not show the same behavior at low pH values as Trisyl. Because Trisyl costs about three times as much as bleaching earth, it was decided to exclude both Trisyl agents from further experiments. No temperature dependence in the extraction of FA was detected in the interval of 65–90°C.

The results from the experiments with pitch revealed that the nickel content could be reduced as efficiently without as with the addition of an adsorbing agent (Fig. 4). In single-stage extraction experiments, the nickel con-

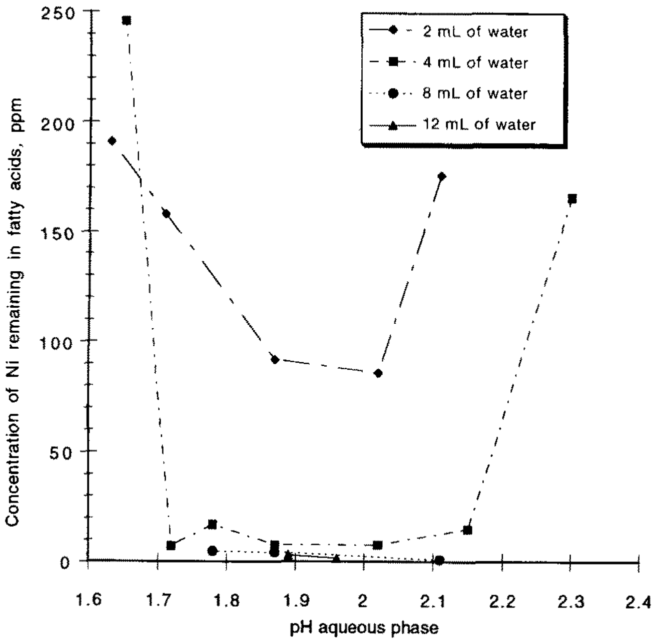

FIG. 2. Concentration of Ni as function of pH with water volume as parameter.

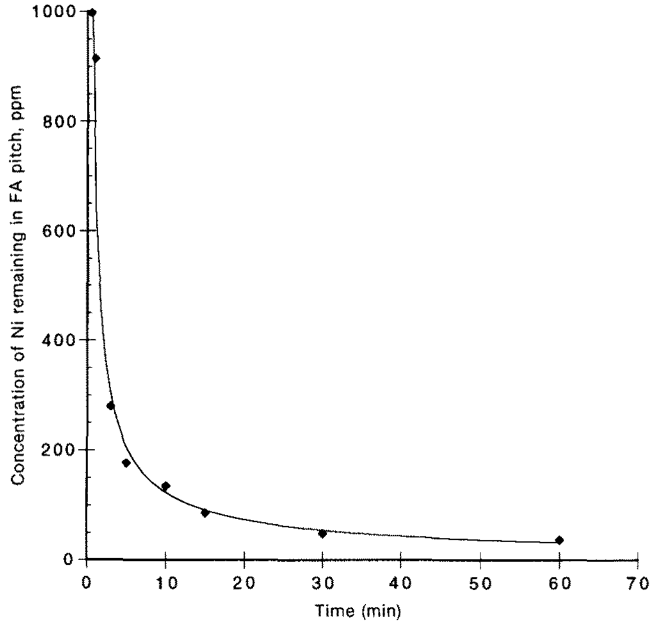

FIG. 3. Concentration of Ni as function of pH with adsorbent agent as parameter. FA, fatty acid.

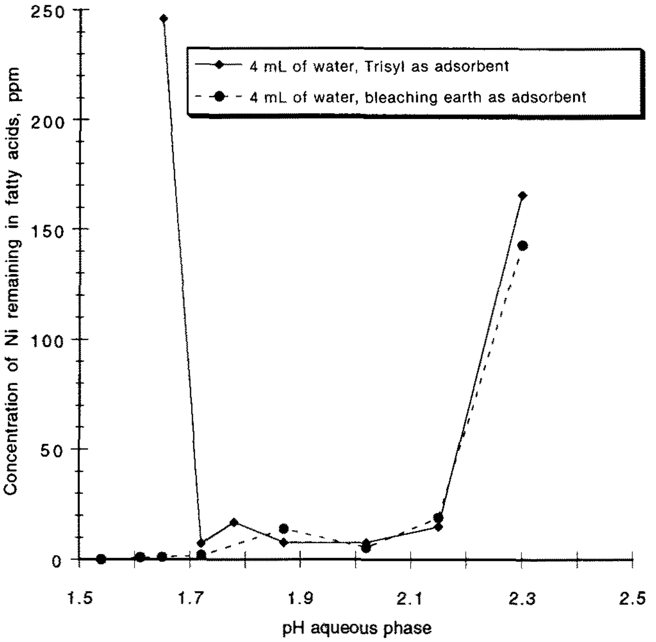

FIG. 4. Concentration of Ni as function of stage number with adsorbent agent as parameter.

tent was reduced from an initial concentration of 2,900 ppm Ni to 49 ppm by using 1.5 mol citric acid/mol Ni and bleaching earth at a concentration of 5 g adsorbent/g citric acid. In double-stage experiments without any adsorbent agents, the nickel content was reduced from 2,900 ppm to 11 ppm by using 1.5 and 64 mol citric acid/mol Ni in the first and second stage, respectively. At a concentration of 3 g adsorbent/g citric acid, the addition of bleaching earth only in the second extraction stage improved the denickling down to 1.3 ppm. However, the citric acid concentration had to be increased to 71 mol citric acid/mol Ni in the second stage. Because material balances showed that only 36–47% of the nickel was adsorbed on the bleaching earth, experiments were performed without adsorption agent. Such an alternative would increase the number of extraction stages needed to achieve the required denickling level, but it would eliminate the use of a filtration step and reduce the risk for clogging the extraction equipment. Accordingly, the nickel content was reduced from an initial concentration of 2,900 ppm Ni to 6.3 ppm in three extraction stages by using 1.5, 21 and 96 mol citric acid/mol Ni in the first, second and third stage, respectively.

Figure 5 shows that the extent of denickling the FA pitch increases considerably with an increase in extraction time. An extraction time of 30 min can be assumed to provide equilibrium conditions for this type of system.

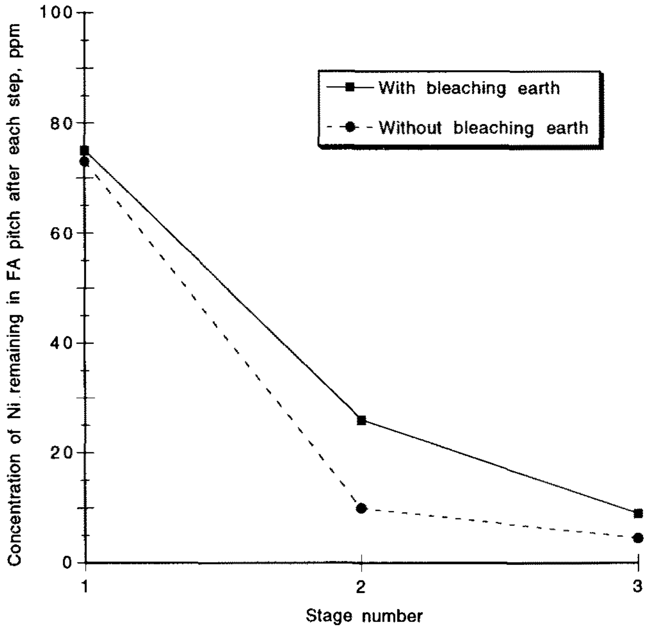

FIG. 5. Concentration of Ni as function of extraction time. FA, fatty acid.

Stripping of Ni from the aqueous phase. An aqueous phase, resembling what was obtained from pitch extraction, was synthesized with a concentration of 4,170 ppm Ni, 3.4 wt% citric acid and a pH of 1.0–1.5. In this study, di(2-ethylhexyl) phosphoric acid (D_2EHPA) and tributylphosphate (TBP) were tested as stripping agents. Both are strong enough to break the Ni-citric acid complexes and form a chelate with Ni. These extractants are usually dissolved in an organic solvent with low solubility in the aqueous phase. Shellsol H, an aliphatic kerosene fraction with 10–30% aromatic content and low solubility in the aqueous phase was therefore selected.

The effects of the stripping agent concentration and the equilibrium pH of the aqueous phase on stripping nickel from the aqueous phase were investigated. A volume of 25 mL of the aqueous phase was extracted at 20°C with 25 mL of the organic phase in the extraction cell for 15 min at 1,000 rpm. The pH of the aqueous phase was varied between 4.0 and 12.5 by adding 1.0 M NaOH solution. Table 1 shows that the best results were obtained with

TABLE 1

Experimental Results of Stripping of the Aqueous Phase^{a}

		pH of aqueous phase		Nickel content (ppm)	
Extractant	Conc. (vol%)	Entering	Equilibrium	Entering	Leaving
D$_2$EHPA	10	4.0	3.9	3,860	3,400
D$_2$EHPA	10	6.1	4.3	3,800	3,200
D$_2$EHPA	25	4.0	3.6	3,860	2,800
D$_2$EHPA	25	6.1	3.8	3,800	2,700
D$_2$EHPA	25	9.9	4.0	3,750	2,800
D$_2$EHPA	25	11.7	4.1	3,720	2,850
D$_2$EHPA	25	12.5	4.4	3,680	2,850
TBP	50	4.0	4.1	3,860	3,800
TBP	50	6.1	6.1	3,800	3,600

^{a}D$_2$EPHA, di(2-ethylhexyl) phosphoric acid; TBP, tributylphosphate.

25 vol% D$_2$EHPA with an equilibrium pH in the aqueous phase of 3.8, where the nickel content was reduced from 3,800 to 2,700 ppm in one stage. In another series of experiments, the nickel content was reduced from 3,650 to 2,200 ppm in three stripping stages with an equilibrium pH in the range of 4.2–4.7. These results were extrapolated in the design of the process flow sheet. It should, however, be stressed that further experimental screening is needed to optimize the stripping step. For instance, the type and concentration of the stripping agent, the organic/aqueous phase ratio, temperature, the equilibrium pH of the aqueous phase and the ionic strength are some process parameters that should be considered in the optimization process.

Acid washing of the organic phase. A diluted mineral acid is usually used as a washing agent to re-extract the metal from the organic phase. An experiment was conducted where 35 mL of Ni-laden organic phase, which was used in the stripping step, was mixed in the extraction cell at 20°C with an equal volume of 0.25 M H$_2$SO$_4$ solution for 15 min. The pH of the acid phase was increased during acid washing from 0.7 to 1.2, and the nickel content in the aqueous phase was reduced from 910 ppm to 460 ppm in one extraction stage. Again, it should be stressed that further experimental screening is needed to optimize the acid washing step. For instance, the type and concentration of the acid washing agent, the aqueous/organic phase ratio, temperature and the equilibrium pH of the acid phase are some process parameters that should be considered in the optimization process.

Flow sheet configuration. The experimental results outlined above were used for the design of a flow sheet, shown in Figure 6, for the denickling process with an annual capacity and operation time of 3,000 ton FA pitch and 6,000 h, respectively. The process was designed based on an initial concentration of 5,000 ppm Ni. Mixer-settlers were selected as extraction equipment because they are essentially simple in design, have a high efficiency, high flexibility, large residence time and low hydrostatic head and are relatively easy to scale up and control. Based on a total efficiency of 75%, four stages ($N_e = 3.0$ equilibrium stages) will be needed in the extraction step, where nickel content can be reduced to 8 ppm. The flow rates of FA pitch and citric acid solution will be 0.567 and 0.514 m^3/h at 80°C, respectively. This would result in a volume of 0.541 m^3 for the mixer and 0.815 m^3 for the settler assuming a residence time of 30 min and a settling area of 1.0 m^2 per stage.

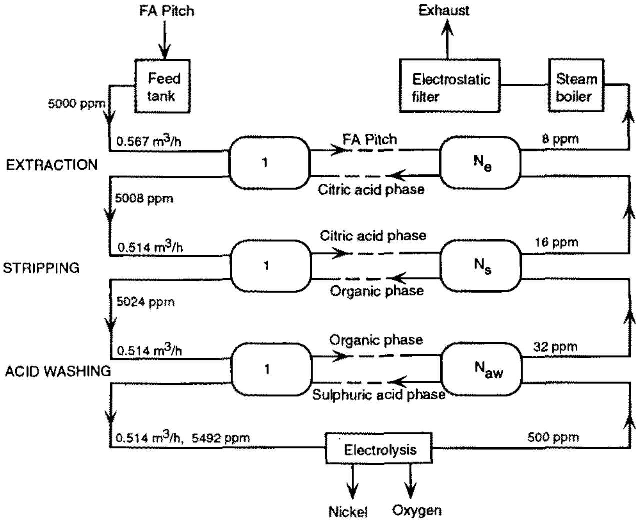

FIG. 6. Schematic flow sheet of the denickling process. FA, fatty acid.

Assuming that the organic phase consists of 50 vol% D$_2$EHPA in Shellsol H and that 50% of Ni will be stripped in each stage, a total of eleven mixer-settler stages ($N_s = 8.3$ equilibrium stages) will be needed in the stripping step to reduce nickel content from 5008 to 16 ppm. Similarly, the acid washing step consists of ten stages ($N_{aw} = 7.5$ equilibrium stages) where 49% of Ni was assumed to be extracted in each stage. The nickel concentration in the organic phase can therefore be reduced from 5024 to 32 ppm. Each stage in both stripping and acid washing steps has a total volume of 0.9 m^3 and a residence time of 15 min in the mixer. Finally, metallic nickel is precipitated in the electrolysis step, where it was assumed that the acid phase concentration is decreased to 500 ppm.

This denickling process has advantageous environmental aspects because it involves three closed-loop liquid cycles and does not use any adsorbing agents. Furthermore, all citric acid losses will end up in the steam boiler together with the denickeled pitch. No preheating of the FA pitch feedstock is needed because it leaves the distillation column at a temperature of 70–90°C. However, the extraction equipment should be thermally insulated and covered to minimize any solvent losses.

TABLE 2

Major Costs for Denickling 3,000 ton Fatty Acid Pitch/Year

Cost item	Extraction	Direct combustion
Fixed capital investment (FCI), k$	2,650	1,310
Loss of chemicals	34	—
Ash disposal	—	10
Electricity and heating	12	—
Maintenance (6% FCI)	156	79
Labor (5 shifts)	90	30
Supervision/laboratory (20% L)	18	6
Direct production costs (k$/year)	310	125
Depreciation (7% FCI)	182	92
Insurance (1% FCI)	26	13
Overheads (40% MLS)[a]	106	46
Fixed charges (k$/year)[b]	314	151
Annual production costs (k$/year)[b]	624	276
Fixed capital investment (k$)	2,650	1,310
Annual income (k$/year)	1,360	1,240
Annual productioin costs (k$/year)	624	276
Specific production costs ($/kg)	0.210	0.092
Pay-off period (years)	3.5	1.4

[a] M, maintenance; L, labor; and S, supervision/laboratory.

[b] The depreciation, insurance and overheads equal the fixed charges, and the fixed charges and the direct production costs equal the annual production costs.

Economic analysis. Both extraction and direct combustion denickling alternatives were economically analyzed. The fixed capital investment was basically provided by equipment suppliers. Direct production costs and fixed charges were calculated according to Kloosterman *et al.* (11) and are given in Table 2 for both alternatives.

(i) *The extraction alternative.* The total fixed cost of a turnkey denickling process according to Figure 6 was estimated to be 2,650 k$. The costs of the extraction-electrolysis equipment, steam boiler (6 MW) and electrostatic filter (for Ni reduction from 150 to 10 mg/Nm^3) were calculated to be 1,417 k$, 833 k$ and 317 k$, respectively. The balance is the cost of chemicals. The cost of energy was based on 0.05 $/kWh for electrical energy and 17 $/ton steam for thermal energy. Saving in fuel oil consumption, partially replaced by pitch, and recovery of metallic Ni are two sources of income generated by this process and were estimated to be 1,240 and 120 k$, respectively. Related to the flow rate of pitch (3,000 ton/year), the specific production cost would be 0.21 $/kg, which is roughly half the price of heavy fuel oil in Sweden. Based on the estimated costs, the pay-off period of this alternative would be 3.5 years.

(ii) *The direct combustion alternative.* The economic data for this alternative are displayed in Table 2 and were based on the same assumptions outlined above. The electrostatic filter is more expensive due to a lower emission level where the Ni-containing dust in the flue gases is reduced to 2 mg/Nm^3. The income from metallic Ni is in this case replaced by a cost of ash disposal. The nickel is enriched in the ash residuals, collected both from steam boiler and electrostatic filter, to a nickel content of 35–40% and must therefore be deposited for long-term storage. The specific production cost and the pay-off period of this alternative would be 0.092 $/kg and 1.4 years, respectively.

The economic analysis revealed that direct combustion is economically more feasible. However, it should be emphasized that some process optimization of the extraction alternative would drastically reduce the total number of mixer-settler stages. For instance, if nickel removal in both stripping and acid washing steps can be increased to 85% per stage, the total number of stages would be reduced from 25 to 12. The fixed cost investment, direct production costs and fixed charges would accordingly be reduced to 1,930 k$, 234 k$/year and 229 k$/year, respectively. The specific production cost and the pay-off period would be reduced to 0.154 $/kg and 2.1 years, respectively. Concerning the direct combustion alternative, the future disposal costs of Ni-rich fly ash are difficult to estimate, and further environmental restrictions may necessitate Ni recovery by a suitable denickling process.

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