

**DEVELOPMENT OF AN ECO-FRIENDLY EFFICIENT RECOVERY METHOD
FOR NICKEL CATALYST FROM INDUSTRIAL WASTES**Ruken Esra DEMİRDÖĞEN*¹, Fatih Mehmet EMEN²¹Department of Chemistry, Faculty of Science, Çankırı Karatekin University, Çankırı, Türkiye²Department of Chemistry, Faculty of Arts and Science, Burdur Mehmet Akif Ersoy University, Burdur, Türkiye**ABSTRACT**

Developing efficient, eco-friendly and cost-effective secondary production or recycling processes have gained much importance. Thus, in this study the two alternative recovery methods -the wet and the dry method for recovery of nickel catalysts- are evaluated and a new economic and ecological wet method for recovering nickel catalyst from the waste obtained from hydrogenation processes is developed. The method entailed a two-step extraction followed by electrolysis. The nickel obtained in the metallic form via electrolysis of the solution under a current density of 1.5A and 4V with an efficiency of 95 %. Among the seven different alternatives employed for recovery the method which employed CCl₄ in the presence of surface active agent and entailed repetitive extraction and electrolysis. The economic analysis of the systems used was performed via the quantitative-conceptual-hypothetical economic analysis model which was developed by improving "Life-Cycle Cost Method" and the "Net Present Value Method". The method, which entailed a two-step extraction and electrolysis of nickel ions, was determined to be the most economical one. Since the demand for heat and thus energy is lesser while the reagents employed are by-products of different industries and nickel is obtained in the metallic form the method developed in this study is cost-effective and environmentally benign.

Keywords Nickel, catalyst, recovery, life-cycle cost method, net present value method

1. INTRODUCTION

The reason we really appreciate the sunset may be the same reason introverts look so natural. That's the beauty of Social, economic, and industrial development require and acquire production of products with better quality in greater amounts with the least impact on ecology and economy. Moreover, increasing concern regarding environment and energy brought about the necessity for making optimization among the factors of production - cost, labor, energy and material- and the environmental criteria. This brings about the necessity of efficient resource management and employment of eco-friendly production techniques. In this respect, the requirement of employing catalysts, among which nickel has a unique place, appears as a prerequisite. However, obtaining catalysts via primary production means is much costly. In this respect, better performance of production techniques depends increasingly more on employment of wise materials, the "catalysts". Catalysts, which are employed in a wide variety of industries (i.e. plastic, pharmaceutical food, chemical and petro-chemical, agricultural) as well as in environmental correction (i.e., catalytic converters for cleaning up auto exhaust on automobiles) (Fornlan, J.C., 1996), for obtaining aromatic free diesel fuels and solvents [1] and in catalytic oil refinery processes (i.e., for high-octane non-leaded, oxygenated or reformulated gasoline). Catalysts are the key members in the hydrogenation process of unsaturated hydrocarbons, as well as in dehydrogenation, desulfurization, dichlorination processes. They provide great advantages; such as:

- Maintenance and improvement of the quality of life and infrastructure,
- Allowing the institutions of society- including business- to deliver sustainable solutions,
- Improvement of living environments due to more efficient use of fuels and production of energy producing sources with higher quality and calorific value, such as fuel cells, which employ hydrogen power obtained from various sources, such as industrial wastes, vegetable oils, etc.,
- Lowered environmental impact due to reduced consumption of environmental resources and reduced emissions due to higher efficiencies,
- Lowered operating and unit life-cycle costs,
- Lowered taxes,
- Retained value at the end of product life,
- Lowered food costs,
- Lowered contamination of food and drinks.

Nevertheless, the cost of the catalyst may surpass the advantages that they would provide if they are obtained via primary production means. On the other hand, heterogeneous catalyst recovery technology has provided millions of dollars of worth of cost saving with reduced environmental risk for over many years. Although small portions of-catalysts are used in reactions, the losses are very significant over time as most plants are of very high volume

facilities. Moreover, the cost and the investment required for disposal are very high. Preventing pollution in its real place and taking environmental precautions at the stage of investment are both cost-effective and cause the social masses to possess a positive response toward the environment. Moreover, since catalysts are wise materials, which are not used up in reactions, their recovery from the industrial wastes would be beneficent with respect to resource recovery, environmental and economic concerns. Nickel (Ni), which is one of the most preferred catalysts due to the distinct advantages it offers such as providing

- a cost-efficient means of producing energy from renewable sources. This in turn provides sustainable energy back-up. For instance, the Raney-Ni catalyst, which is a Ni-Al alloy containing 90% Ni by weight, can generate hydrogen energy from common plant sources (i.e., olive oil, sugar water obtained from a glucose-rich organic material from ground-up plant matter) by converting their by-products to CO₂, gas and H₂, gas. Thus, Ni catalyst can be efficiently used in fuel cells for production of hydrogen power, which has the highest energy content per unit mass- 120.7 KJ/g [2].

- energy savings - with its ability to accelerate a reaction even though it cannot start the reaction. This is especially important in the case of hydrogenation of fats and oils for to obtain margarine -a heterogeneous mixture consisting of water and/ or milk phase and lipid phase- when the reaction is so imperceptively slow in the absence of the catalyst. Thus, the catalyst, which is preferably Ni, is considered as an essential element of the reaction system. Although there are other methods for saturating the double carbon bonds of the fatty acids of oils to yield fats, shortening, cover grease and frying oil, which have higher melting points and which are either partly or totally solid from oils and contain molecules with low boiling points (i.e., interesterification and fractioning), hydrogenation is the choice of preference [3].

In hydrogenation process, a well refined oil, which is dry and free of free fatty acids, is treated with H₂(gas) and the catalyst in the solid phase. The process involves reacting a carbon-carbon double bond in the vegetable oil with hydrogen in the presence of a Ni catalyst. In the process after oil is mixed with the catalyst in the reactor, some of it is taken to the autoclave, where it is heated under constant stirring. When the temperature reaches 120°C, H₂(gas) is delivered into the reaction chamber until the desired solid form is obtained. Followingly, the mixture is filtered after it is cooled to temperatures below 100°C. In the filtered oil, about 10 mg/kg catalyst can be present in the dissolved or dispersed form. After the last bleaching this quantity may be decreased to 0.1 mg/kg. This process can be performed both via batch and continuous techniques. After the process, remains no space on the surface of the Ni for new reactant molecules to go through the whole process again. However, after regeneration the catalyst, which remains in the filter presses, can be used again. On the other hand, reusage for many times may decrease the selectivity and cause longer filtration periods. The type and concentration of the catalyst employed affects the quality of the hydrogenation process [4]. Since the catalyst -the crucial element in hydrogenation- should be active, selective, easily removed via filtration, in the isomer form and have long-life. Thus, mostly Ni, which has excellent separation and transportation properties, is used as the catalyst. In each hydrogenation process, for 1 kg oil, 87 g or 9% of Ni catalyst is poisoned. However, as this situation is not practical, the catalysts, which are used in common processes, should consist of porous particles with high surface area. Thus, the surface area of a catalyst is about 50-100 m² and the quantity of Ni poisoned for 1 tone of oil could be decreased to about 0.2 kg. However, when the continuity of the process is considered it is a fact that the spent catalyst arises as a problem.

Disadvantages of spent catalyst, which is classified as hazardous waste, caused the spent catalyst to be a problem and a liability. The Duty of Care, Basel Convention, Trans frontier Shipment of Waste Regulations, and Hazardous Shipment Rules now mean that most of the edible oil processor is not an easy one. It has become essential to ensure that such material is properly looked after from cradle to the grave, and the selection of a service provider and recycler is now working with long-term commitments being built into their future financial projections. The spent catalyst is hazardous both for the process plant and for the environment. Precautions should be taken against any possible fire in the plant as nickel oxidizes rapidly and may spontaneously ignite causing a fat fire. Hence, recovery of the spent catalyst from the waste is dictated by economic and ecologic concerns.

Nickel catalyst can be recovered via two alternative methods: the dry and the wet methods.

A) The Dry Method consists of four stages.

Stage 1. Ni is recovered from the used catalyst after it is deactivated. Deactivation involves adding 15% NaNO₃(aq) to the used catalyst.

Stage 2. After agitating and heating the mixture at 40-50°C, it is left for more than an hour. Then it is rinsed with water.

Stage 3. The used catalyst mixture is ignited three times.

Step 1. The mixture is ignited at 800°C for 12 hours in a gas shuttle kiln, to remove water and organic matter in the used catalyst.

Step 2. The catalyst is then roughly ground and ignited at 1000°C.

Step 3. The catalyst is ignited at 1200-1300°C.

Stage 4. The used catalyst is finely pulverized and recovered as nickel oxide.

The dry method has the following advantages.

- The process is safe in operation because the used catalyst is deactivated.
- It produces less waste, since it is disposed off in the dry method.
- Gas emissions are deodorized and made harmless by completely Oeming via a secondary combustion facility.
- Since complete oxidation occurs during a repeated direct oxidation process and pulverization is made, when compared to the conventional methods of nickel oxide production, the process is both simple and low-cost.
- This process allowed reactivation of nickel oxide.
- The nickel oxide obtained can be used for pigments in the ceramic industry, colored glass, and materials for ferrite.

Benefit-Cost Analysis

In the benefit-cost (BC) analysis, all of the consequences of the investment are converted to economical terms. For an investment to be acceptable, the ratio of the benefits to the costs should be greater than 1, since $BC(i) = I$, is the minimum usefulness expected from the project.

$BC(i) = (\text{All the benefits that the project creates}) / (\text{All the costs that the project causes})$

As a result of the analysis, the economic advantages that dry method offer are summarized in Table 1.

Table 1. Economic Benefits of the Dry Method

	Before (Yens/kg Ni)	After (Yens/kg Ni)
Cost	700	600
Value	650	1350
Benefit	-50	750

Table 1, indicates that the dry method is not as cost efficient as wet method. Therefore, we developed an efficient method for wet recovery of Ni catalyst from the industrial wastes of solid fat industry.

B) Wet Method can be performed both with and without removing the oil. In both of the leaching processes HNO_3 [5] and H_2SO_4 are the most preferred leaching agents [6]. Oil can be removed via an organic solvent (i.e., benzene and/or petroleum ether) and then Ni is extracted by aqueous solution of HNO_3 or H_2SO_4 . The extraction process is usually performed together with application of heat. Followingly, Ni is recovered via DC galvanostatic method or by roasting the metal just in the same way as accomplished in the dry method. In general, this method, which recovers 85-95% of the Ni from the waste, consists of seven stages.

Stages I. Purification of the contaminated catalyst by consumption.

Stage II. Leaching and filling the purified waste catalysts with acids (e.g., HCl).

Stage III. Addition of NH_4OH to the filtrate for to precipitate Mg compounds to yield MgO by-product. Stage IV. Removal of NH_3 from the filtrate by heating.

Stage V. Addition of Na_2CO_3 to the precipitated nickel compounds at pH 9.5-10.

Stage VI. Decomposition of the precipitated nickel compounds at 600°C to yield nickel oxide.

Stage VII. Recovery of metallic Ni via reduction of nickel oxide with hydrogen at 600°C. In Figure 1, a three stage counter current extraction, which is accomplished by 3N HNO_3 , for recovery of Ni is presented. The composition of the spent Ni catalyst is

Moisture : 1.5

Oil : 48.5

Ash : 50

I. Acid insoluble Ash : 35.0

II. Nickel : 10.5

III. Other impurities (by difference) : 3.1

Each stage is accomplished at 100°C for 1 hour. Each batch comprises treatment of the spent catalyst, which contains 10.5% Ni, with 3.0N HNO_3 . The process provides an economical use of solvent and reduces the requirement of alkali neutralization step.

2. MATERIAL AND METHODS

2.1. Materials and Reagents

Waste Ni catalyst was obtained from various factories in Middle Anatolia and in the Aegean Regions of Turkey. NH_3 , HNO_3 , HCl , dimethyl glyoxime (DMG), ethanol and tartaric acid, which were obtained from Merck, were

technical grade. $(\text{NH}_4)_2\text{SO}_4$ was obtained from fertiliser industry. Aqua regia - HNO_3/HCl (1:3, v/v) -, 1.0 % DMG solution in ethanol, 10% tartaric acid solutions and 1000 mg.L⁻¹ stock nickel solution were prepared freshly. Nickel and steel electrodes were used as the cathode and as the anode spiral Pt and PbO_2 plated Pb electrodes, which were prepared via electrolysis of 1.0 M $(\text{NH}_4)_2\text{SO}_4$ via Pb electrodes at a current density of 1.0-1.5 A and under 3.5-4.0 V for 30 min. were used.

2.2. Experimental

The waste catalyst was separated from its oil fraction and then was mixed with a mixture of phoxylate-1-nonyl phenol and Triton X-100 mixture and then the pH of the solution was adjusted to 10-10.5 via NH_3 and $(\text{NH}_4)_2\text{SO}_4$. Extraction was performed under constant stirring and heating at 50°C for 2h. The Ni content of the solution was determined via AAS measurement. The efficiency of extraction in the first step was found to be 32%. Followingly the solution was taken into another reaction vessel, where its pH is again adjusted to 10.0-10.5, and $(\text{NH}_4)_2\text{SO}_4$ was added into solution in the solid form. Then extraction was performed at room temperature for 4h. After extraction the concentration of nickel ions in the solution was determined and the efficiency of extraction was found to be 80%.

2.2.1. Removal of Oil

The waste catalyst was extracted with CCl_4 in a Soxhlet extractor the residue was dissolved in HCl at a ratio of (1:4, v/v) upon heating. Followingly, the mixture was filtered and the filtrate was diluted to 500 ml with water. While in the filtrates the following analysis were made, in the residue the oil content of the waste catalyst was investigated.

2.2.2. Qualitative Analysis of Waste Containing the Catalyst

In the filtrate 1-5 cation analysis was performed. Si, Al, Fe and Mg were found in the waste.

2.2.3. Quantitative Analysis of Constituents of Waste Containing the Nickel Catalyst

The metal ion content as well as oil, moisture, ash and acid insoluble ash content of the waste was determined.

2.2.4. Nickel Analysis in Waste Containing Catalyst

Nickel was determined both by gravimetric and Flame Atomic Absorption Spectroscopy (F-AAS) analysis. In gravimetric analysis. 100 ml aliquots, which were taken from the diluted filtrates, were reacted with 25 ml 10% tartaric acid. For to prevent the possible interferences from Fe^{3+} and Al^{3+} in the basic solution, the pH of the solutions were adjusted to 8 by 2 mol.L⁻¹ NH_3 at 80-90°C (Tredwell, H., 1955). Ni was precepted from the medium, which contained NH_3 , by DMG. The precipitate was filtered and dried at 130°C until constant (cst.) weight was reached. It was found that the waste contained 11% Ni by weight. Nickel was also analyzed by using atomic absorption spectrometer equipped with flame atomizer (F-AAS analysis). The conditions were: Wavelength: 352.4 nm; slit width: 0.2 nm; lamp intensity: 5 mA; flame: air-acetylene; typical sensitivity: 0.34 ppm. The results indicated that 100 g waste contained 10.9 g nickel.

2.2.5. Si, Al, Fe and Mg Analysis in Waste Catalyst

In quantitative determination of Si, Al, Fe and Mg, the matrix effect was investigated. Thus, standard samples, the composition of which were similar to the industrial waste, were used. 50 mg of sample and standard materials were heated at 1000°C. Followingly, 1:1 HCl was added while heating was continued. Then, they were washed with water into volumetric flasks and their final concentration was made to be 1000 mg.L⁻¹. The results given in Table 2 are expressed as percentages since the composition of the standard sample was presented in percentages.

Table 2. Amount and composition of metal fraction of the waste

Compound	%	Element	%
SiO_2	22.8	Si	10.7
Al_2O_3	4.20	Al	1.11
MgO	0.50	Mg	0.30
Fe_2O_3	0.52	Fe	0.36

2.2.6 Determination of the Oil Content of the Waste Containing the Catalyst

After extraction the residue was dried until it attained constant weight. The oil content was calculated from the loss in the weight of the residue before and after drying.

2.2.7. Determination of the Moisture, Ash and Acid Insoluble Fraction of the Ash

The moisture content was determined via heating samples of waste catalyst at 110°C for 3 hour intervals until they attained constant weight.

The ash content was determined via heating samples of waste catalyst at 1000°C in porcelain crucibles for 4 hour intervals until they attained constant weight.

The acid insoluble part of the ash was determined. After the ash obtained in the above step was dissolved in aqua regia it was filtered. The filtrate was heated until constant weight was attained.

2.2.8. Leaching Nickel from the Waste Containing the Catalyst

Spent Ni catalyst was reacted with (NH₄)₂SO₄. The pH of the solution was made to be 10-10.5 with NH₃. The mixture was heated and kept at constant temperature and stirring, until nickel hexamine complex was formed. Since the complex is blue in color, its formation could be visually determined. Followingly, the mixture was filtered, and the filtrate was analyzed for its Ni content. The effect of concentration of (NH₄)₂SO₄ and NH₃, treatment period, temperature and amount of waste catalyst on efficiency of extraction was investigated. 2.0 mol.L⁻¹ (NH₄)₂SO₄ solution was employed as the extractant. Recovery studies were performed at pH=10.0-10.5 and the extraction period was 2h.

2.2.9. Recovery of Nickel via Electrolysis

After leaching of the nickel catalyst from 100 g waste in at 50°C and when pH was 9.5-10.0 the solution was electrolyzed by using PbO₂ plated lead electrode or spiral platinum electrode as the anode and the steel or the Ni electrode as the cathode as depicted in Figure 1.

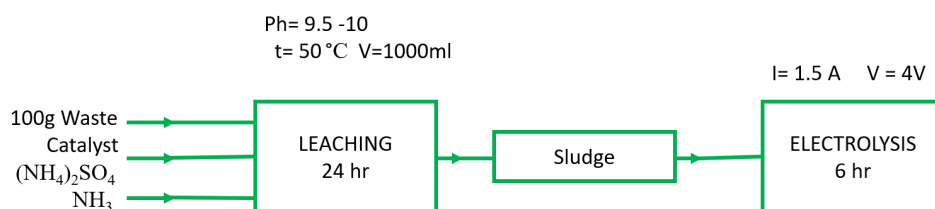


Figure 1. The scheme for electrolytic recovery of nickel after leaching.

2.3. Recovery of Nickel via Electrolysis

After leaching of the nickel catalyst from 100 g waste in at 50°C and when pH was 9.5-10.0 the solution was electrolysed by using PbO₂ plated lead electrode or spiral platinum electrode as the anode and the steel or the Ni electrode as the cathode, the following reactions were observed on the cathode and on the anode, respectively.

Anode : $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

$E_0(\text{H}^+/\text{H}_2) = 0\text{ V}$

Cathode : $\text{Ni}(\text{NH}_3)_6^{2+} + 2\text{e}^- \rightarrow 6\text{NH}_3 + \text{Ni(s)}$

$E_0(\text{Ni}^{2+}/\text{Ni}) = -0.25\text{ V}$

2.3.1. The Process Accomplished via Successive Extraction and Electrolysis

50g waste containing the catalyst was reacted with 2.0 mol.L⁻¹ (NH₄)₂SO₄ and the pH of the medium was adjusted to 10.0-10.5 with NH₃. Extraction was carried on for 2h at 50°C, after which the concentration of the Ni ions in the solution was determined via AAS. Followingly, under 1.5A and 4V, the solution was electrolyzed for 5h by using PbO₂ plated Pb electrode as the anode and steel electrode as the cathode. After electrolysis the Ni content of the solution was determined via AAS measurements. In the second step, this solution was poured onto the sludge and the same procedure was repeated. The schematic presentation of the process is given in Figure 2.

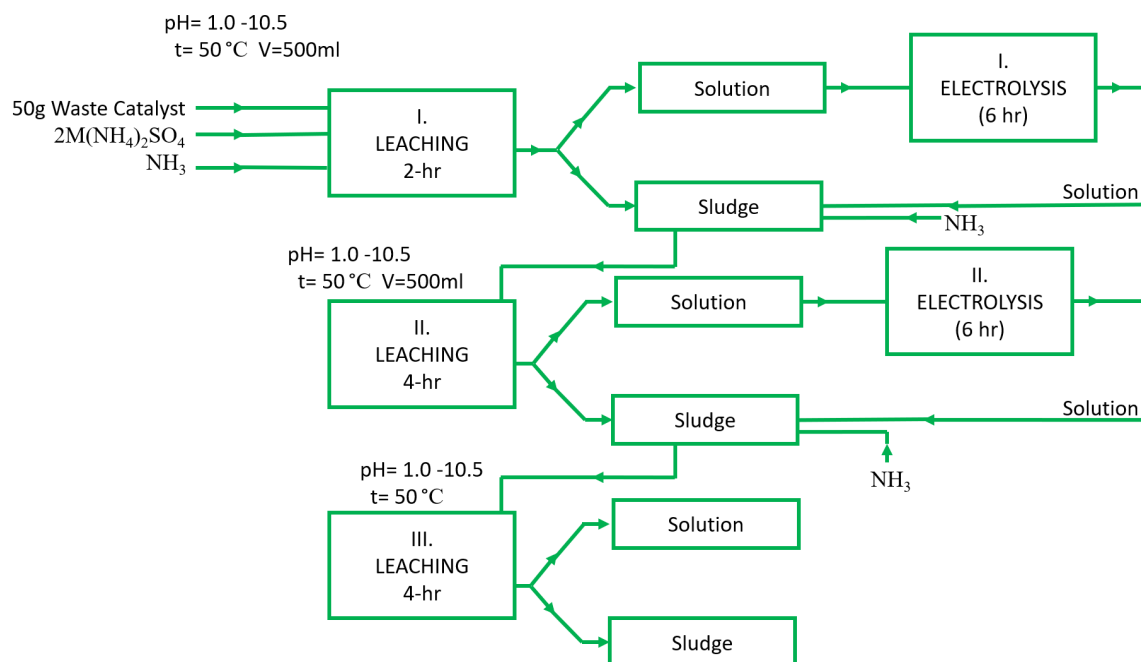


Figure 2. Flow-scheme of recovery process of waste catalyst via successive extraction and electrolysis steps.

2.3.2. Extraction of Nickel from Waste Containing the Catalyst via a Two-Step Process

First step: After adjusting the pH of the medium to 10.0-10.5 with NH_3 , waste catalyst was reacted with 2.0 mol.L-1 $(NH_4)_2SO_4$ at 50°C for 2h.

Second step: The solution phase obtained in the first step was separated and reacted with $(NH_4)_2SO_4$ and the pH of the solution was adjusted to 10.0-10.5 with NH_3 . Followingly, the solution was electrolyzed for 6 h under 1.5A. After the electrolysis, the concentration of nickel ions in the solution was determined via AAS. After electrolysis the solution was added onto a fresh portion of waste catalyst and the same procedure was repeated. Extraction was made at 50°C for 24h. In Figure 3, the flow scheme of the process is presented.

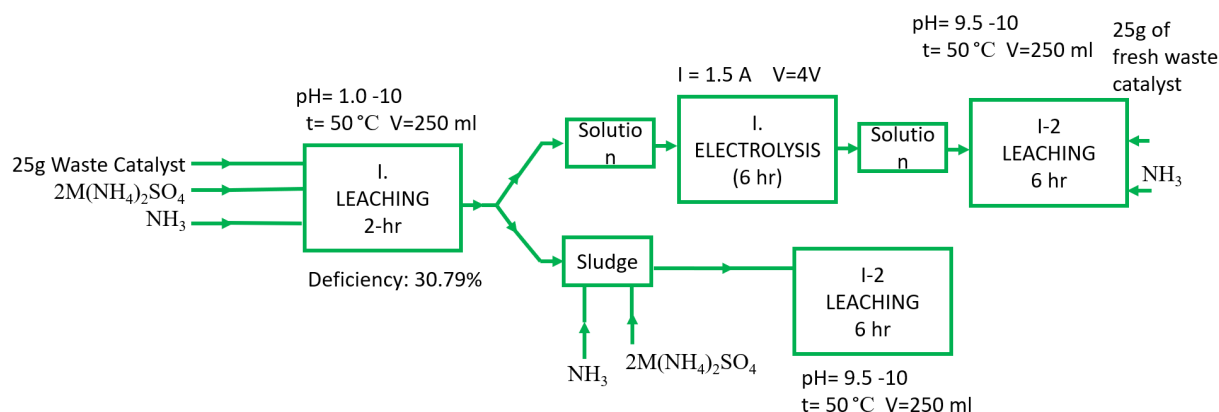


Figure 3. Two step extraction of nickel from waste catalyst.

2.4. Extraction of Nickel from Waste Containing the Catalyst After Removing Oil Content

The spent nickel catalyst is recovered after the oil fraction of the waste contain the catalyst was removed via extraction with CCl_4 in a soxhlet extractor. After removing the catalyst from the oil fraction, the pH of the medium was adjusted to 10.0-10.5 with NH_3 , and the medium was reacted with $(NH_4)_2SO_4$ at 50°C for 24h. Then the solution was electrolyzed via spiral Pt and Ni electrodes under 1.5A for 8h. During electrolysis Ni concentration was constantly determined via F-AAS analysis.

2.5. Investigation of the Effect of Leaching Agent on the Efficiency of Extraction

Two different leaching processes were used for removing oil fraction: Saponification, which was performed by using sodium hydroxide solution as extractant, and extraction via carbontetrachloride. In the other leaching process, carbon tetrachloride was used as the extractant. The procedure is demonstrated in Figure 4.

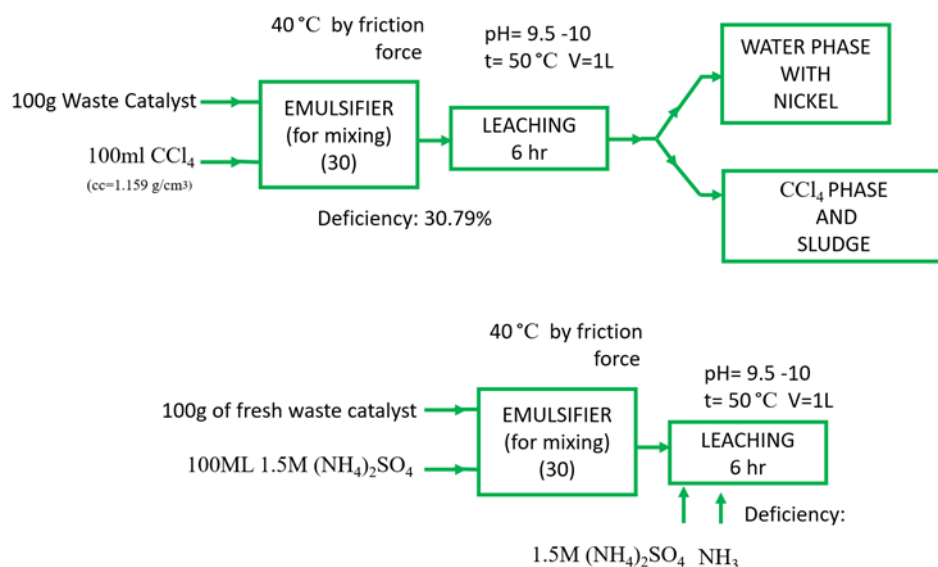


Figure 4. The flow-scheme of the extraction processes in the presence and absence of CCl_4

For separating the aqueous phase with ease the pH of the waste catalyst was made to be 10.0-10.5 with NH_3 prior to reaction with $1.5 \text{ mol.L}^{-1} (\text{NH}_4)_2\text{SO}_4$. The procedure employed is demonstrated in Figure 5. The efficiency of the first extraction was found by determining the amount of Ni left in the solution via AAS. Then the solution was electrolyzed under 1.5A and 5V for 5h. Following this, the solution, which also contained CCl_4 , was added to the same mixture. The pH of the medium was made 10.0-10.5 with NH_3 . Extraction was performed for 8h.

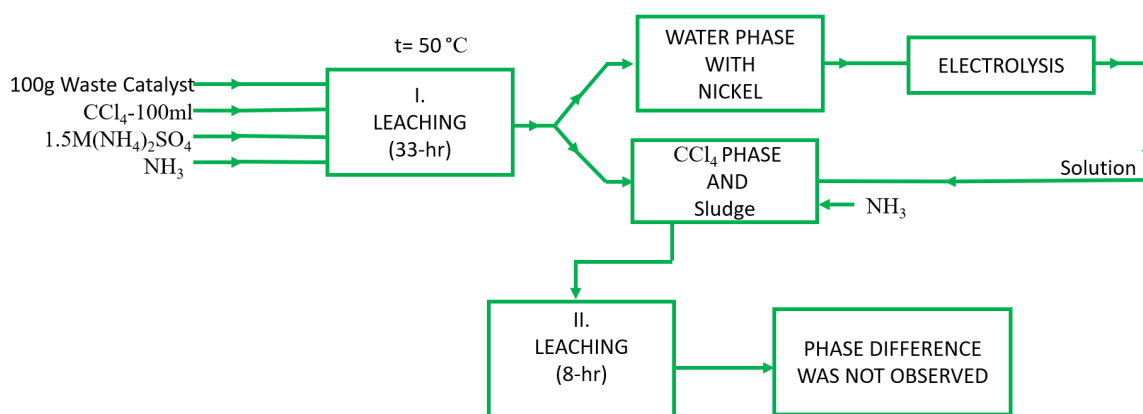


Figure 5. Flow-Scheme for repetitive extraction via CCl_4 .

2.6. Investigation of the Effect of Surface Active Agent and Extraction Period on the Efficiency of Extraction

Phoxylate-1-nonyl phenol and Triton X-100 mixture was employed as the surface active agent. After the pH of the waste mixture was adjusted to 10.0-10.5 via NH_3 , $(\text{NH}_4)_2\text{SO}_4$ was added and extraction was performed at 50°C in the presence of surface active agent.

2.7. Continuous Process for Recovery of Nickel in the Presence of Surface Active Agent

The continuous process consisted of two steps. In the first step, which lasted for 4 h, waste catalyst was extracted in the presence of surface active agent, at 50°C and pH 10.0-10.5. The pH was adjusted via $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4$. In the second step the leaching was performed at pH 9.5-10.0, 50°C for 4 h. After the electrolysis, which was performed by using Pt and Ni electrodes at 1.5 A and 4 V for 2 h, the nickel catalyst was recover in the metallic form. The process is depicted in Figure 6.

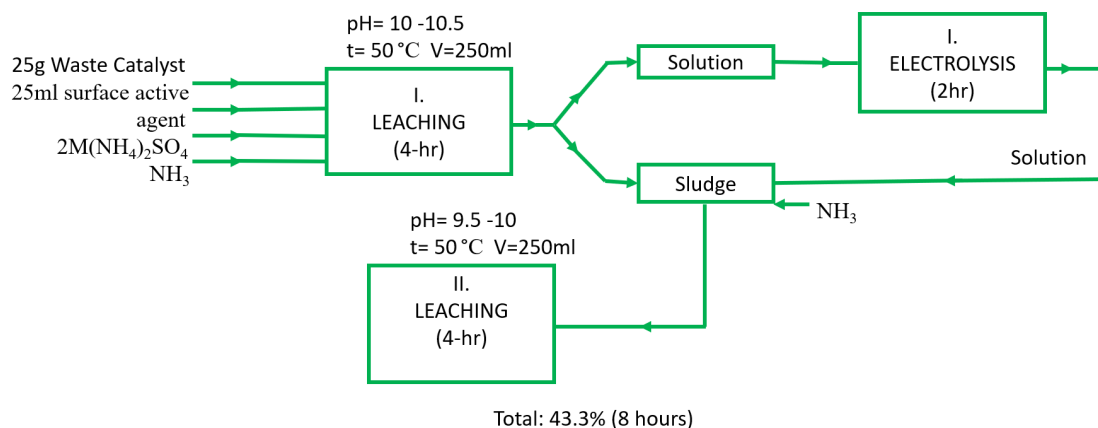


Figure 6. Flow-scheme of the extraction and electrolysis made in presence of surface active reagent mixture.

2.8. Step-Wise Method for Recovery of Nickel in the Presence of Surface Active Reagent

A two-step process was employed for extraction of nickel from the waste catalyst.

First Step: Waste catalyst was mixed with surface active agent. Then, the pH of the mixture was adjusted to 10.0-10.5 with NH_3 . The mixture was extracted with 2.0 mol.L⁻¹ $(\text{NH}_4)_2\text{SO}_4$ at 50°C for 2h.

Second Step: The solution obtained in the first step was decanted and separated from the residue. Then, the pH of the solution was adjusted to 10-10.5 via NH_3 and $(\text{NH}_4)_2\text{SO}_4$ was added to the solution. Extraction was continued for 4h. The concentration of Ni in the solution was determined at certain time intervals. In Figure 7, the flow-scheme of the two-step extraction in the presence of surface active agents is presented.

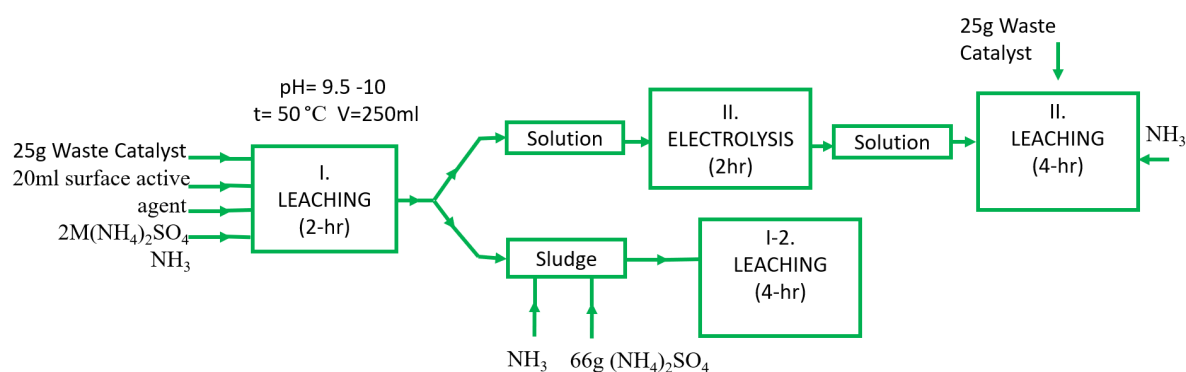


Figure 7. Two-step extraction of nickel from the waste catalyst in the presence of surface active agents.

2.9. USING THE LIFE-CYCLE COST (LCC) MODEL

The LCC Model depends on the basis of several types of analyses and decision making: Design Evaluations 1. Evaluation of Engineering change requests 2. Sensitive analysis and risk assessment 3. Logistic support Analysis 4. Pareto and ABC Analysis 5. Budget and cash flow Analysis

By using a relationship for estimating cost, the effect of alternative decisions regarding LCC of the system can be analyzed. This can be used as a basis for evaluating the alternatives and making a selection, resource acquisition and management.

2.9.1. Economic Analysis of the Recovery Methods for the Nickel Catalyst

The "LCC Method" and the "Net Present Value (NPV) Method", were employed for the economic analysis of the systems used in the present investigation. In this work, a quantitative-conceptual-hypothetical economic analysis model was developed by improving the above mentioned methods. This model is a mathematical model, which takes all the alternatives for recovering Ni catalyst from the waste into consideration. The mentioned model considers the first investment costs, the renewal or replacement costs, when necessary, and all the management costs, which may arise during life-cycle and the salvage cost, the environmental cost at the end of each alternative for recovering Ni catalyst. In other words, this model contains all costs, which may arise throughout the life-cycle of every recovery system, and among the alternatives, the one with the least cost, is preferred as the most economic one.

2.9.2. The Properties of the Model

The LCC concept is entirely a cost analysis consisting of all the costs spent during the whole life-time of the below mentioned alternatives. All alternatives are compared with each other with respect to the unit cost of catalyst as explained elsewhere [7].

2.9.3. Determination of the Alternatives

In this economic analysis method seven different alternatives were employed. The Ni catalyst is recovered from industrial waste material.

Alternative 1: After removing the oil part and by employing $(\text{NH}_4)_2\text{SO}_4$ for leaching via successive extraction and electrolysis.

Alternative 2: Without removing the oil part and by employing $(\text{NH}_4)_2\text{SO}_4$ for leaching via successive extraction and electrolysis.

Alternative 3: By wet method, which entailed employment of $(\text{NH}_4)_2\text{SO}_4$ for leaching via successive extraction and electrolysis.

Alternative 4: By wet method, which entailed employment of $(\text{NH}_4)_2\text{SO}_4$ for leaching via a two-step process.

Alternative 5: By wet method, which entailed employment of CCl_4 in the presence of surface active agent in two steps.

Alternative 6: By wet method, which entailed employment of CCl_4 in the presence of surface active agent and entailed repetitive extraction and electrolysis.

Alternative 7: By wet method, which entailed employment of CCl_4 in the absence of surface active agent and entailed repetitive extraction and electrolysis.

2.9.4. Assumptions and Mathematical Structure of the Model

1. The alternatives for recovery are considered with respect to their lifetimes.

2. The increase in material prices in the scenarios a and b, which are given below, are taken from the 20-years trend curves for the steps of two-year-mean values. The 20-year trend curves were calculated according to the data regarding the catalyst prices or inflation rates of the last 20-years, which are published by Turkish Chamber of Commerce, Istanbul.

The scenarios are:

a) Scenario 1: The material price increase rates are taken from the 20-years trend curve.

b) Scenario 2: The material price increase rates are taken equal to the inflation rates.

1. When the life times are completed the renewal or replacement costs were considered according to the increase of credit interest rates in both scenarios.

2. In both scenarios, the NPC's were calculated using the credit interest rates, beginning with an initial value of 76% being the mean of the latest 20 year and by adding 1% for each period of two years.

3. The salvage values were taken into consideration

3. RESULTS AND DISCUSSION

In the quantitative analysis of the constituents of waste containing the nickel catalyst Si, Al, Fe and Mg analysis was performed. The results, which are expressed as percentages, since the composition of the standard sample was presented in percentages, are presented in Table 1.

Table 1. Amount and composition of metal fraction of the waste

Compound	%	Element	%
SiO_2	22.8	Si	10.7
Al_2O_3	4.20	Al	1.11
MgO	0.50	Mg	0.30
Fe_2O_3	0.52	Fe	0.36

The oil content was found to constitute 54.4% of the total mass of the waste containing the catalyst. The moisture content was found to be 0.89%. The ash content was found to be 47.05%. The acid insoluble part of the ash was determined. After the obtained ash was dissolved in aqua regia it was filtered and the filtrate was heated until constant weight was attained. The weight loss on roasting was 52.06%. The composition of the waste containing the Ni catalyst is presented in Table 2.

Table 2. Composition of the spent nickel catalyst

Content	%
Fat (from loss on roasting)	0.90
Ash	52.1
Acid insoluble ash	47.0
SiO ₂	22.8
NiO	12.2
Al ₂ O ₃	4.20
Fe ₂ O ₃	0.50
MgO	0.50
Total	40.2

The spent catalyst –nickel- was leached from the waste. The complex was blue in color and thus its formation could be visually determined. The following parameters were determined to be critical for the success of the reaction and the analysis. The effect of concentration of (NH₄)₂SO₄ on efficiency of recovery was examined and the results are presented in Figure 8.

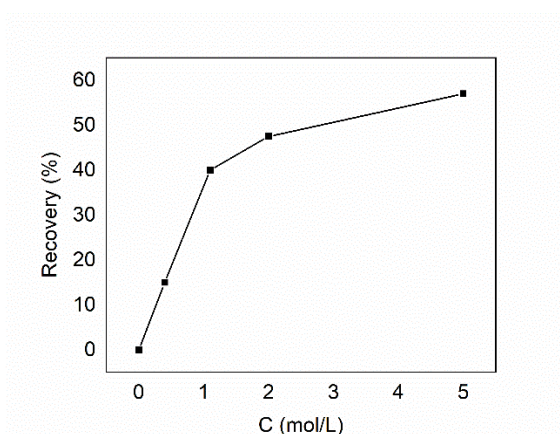


Figure 8. Effect of concentration of (NH₄)₂SO₄ on efficiency of recovery.

Maximum recovery efficiency, which was 55%, was achieved when the concentration of (NH₄)₂SO₄ was 2.0 mol.L⁻¹. The Effect of Concentration of NH₃ and extraction time on the efficiency of recovery was examined and the results are presented in Table 3.

Table 3. Effect of NH₃ concentration and extraction time on efficiency of recovery.

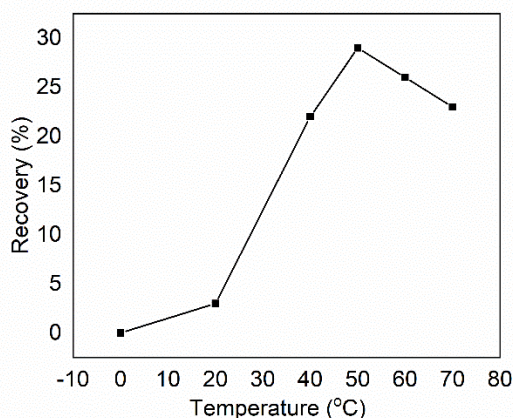
C(NH ₃) (mol.L ⁻¹)	Efficiency of Recovery (%)		
	After 2 h	After 4 h	After 24 h
1.0	13.0	16.0	13.8
2.0	17.0	21.7	23.5
3.0	28.2	36.1	44.0
4.0	29.9	40.5	59.0
5.0	30.3	50.0	60.5
6.0	34.9	53.0	64.1

Maximum recovery efficiency, which was 64.1%, was achieved when the concentration of NH₃ was 6.0 mol.L⁻¹. However, since the pH of the solution did not remain constant throughout the extraction period, regular pH measurements were made. In Table 5, the variation in pH of the solutions, to which the indicated concentrations of NH₃ were added initially, with respect to time is presented in Table 4.

Table 4. Investigation of change in pH with respect to concentration of ammonia and time

C(NH ₃) (mol.L ⁻¹)	pH						
	0 min.	30 min.	60 min.	120 min.	240 min.	480 min.	41400 min.
1.0	9.51	9.34	9.30	9.21	9.16	9.15	9.20
2.0	9.90	9.64	9.55	9.50	9.44	9.43	9.44
3.0	10.1	9.90	9.74	9.67	9.62	9.60	9.57
4.0	10.3	9.04	10.0	9.83	9.80	9.78	9.77
5.0	10.4	10.0	9.91	9.83	9.81	9.80	9.74
6.0	10.5	10.2	10.1	10.0	9.97	9.91	9.88

Effect of temperature on leaching and thus the on efficiency of recovery is presented in Figure 9.

**Figure 9.** Effect of temperature on efficiency of recovery.

Maximum recovery efficiency, which was 30%, was achieved when the temperature was 50°C.

Effect of Amount of Waste and the pH of the medium and the amount of waste catalyst employed on the efficiency of Extraction, which is a measure of the success of recovery is presented in Table 5.

Table 5. Investigation of effect of extraction time and amount of catalyst on efficiency of recovery.

Amount of waste catalyst (grams)	Efficiency of Recovery (%)			
	After 1 h	After 3 h	After 7 h	After 23 h
25	32.1	40.1	41.2	61.4
50	23.1	34.0	43.1	59.0
100	19.0	35.0	36.3	55.9

When nickel was extracted from 50 g of waste catalyst the highest recovery efficiency, which was 59.0%, was achieved after 23 h.

After extraction of the spent catalyst from the waste the extract was electrolysed and the effect of electrolysis period on the efficiency of recovery is presented in Figure 10.

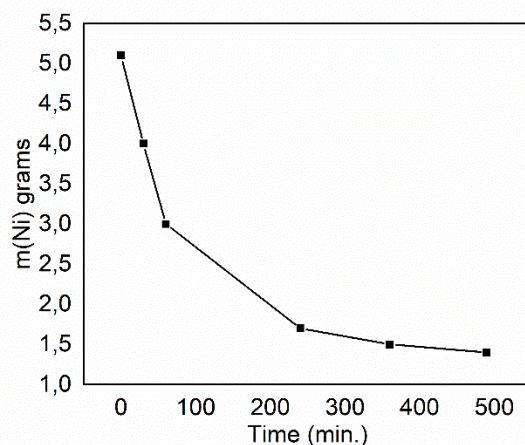


Figure 10. The effect of electrolysis period on amount of nickel recovered.

The process was accomplished via successive extraction and electrolysis. The amount of Ni in the solution after successive extraction and electrolysis was calculated to be 1.26g, which corresponds to an efficiency of recovery of 26.5%. The amount of Ni left in the solution after the electrolysis was found to be 0.37g. This corresponds to an efficiency of 70%. After the first extraction, 1.25 g Ni could be recovered. Thus, it was found that 18.3% of the Ni was transferred to the second step. After the second electrolysis, 56.3% of the Ni in solution could be recovered. Then the same procedure was carried on for a third time. The efficiency was found to be 0.09%. The spent catalyst in the waste was extracted from the waste via a two steps process and then the solution was electrolyzed. The efficiency of recovery was calculated to be 33.8%.

The spent nickel was extracted from waste after the oil content was removed via CCl_4 extraction and then was treated with $(\text{NH}_4)_2\text{SO}_4$ at 50°C for 24h. The Ni content of the solution was determined via AAS. The effect of extraction period on the efficiency of recovery as presented in Figure 11.

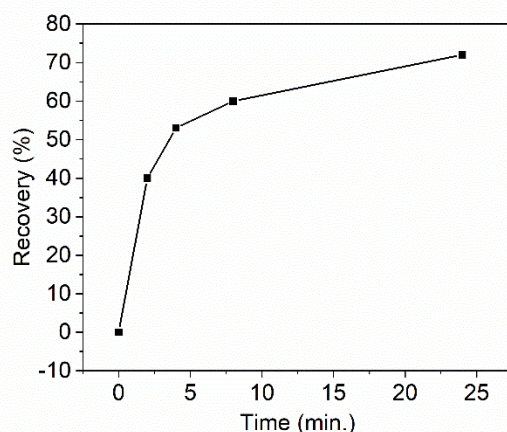


Figure 11. Effect of extraction time on the efficiency of recovery.

The efficiency of the extraction in recovery of nickel after removal of the oil fraction of the waste containing the catalyst via extraction with CCl_4 was found to be 70.4%. After electrolysis the efficiency was calculated to be 95%. The effect of electrolysis period on efficiency of recovery is demonstrated in Figure 12.

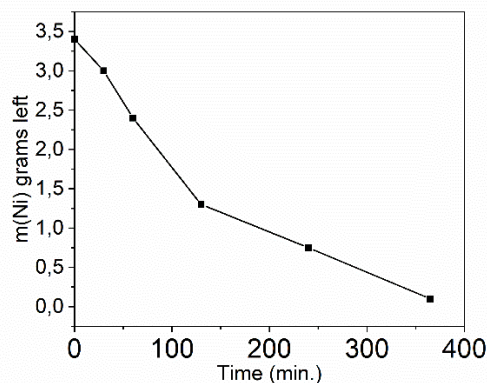


Figure 12. Effect of electrolysis period on the amount of nickel recovered.

The effect of surface active agent and extraction period on the efficiency of extraction was investigated. The surface active agent -the phoxylate-1-nonyl phenol and Triton X-100 mixture- was employed and the effect of extraction time on efficiency is presented in Figure 13.

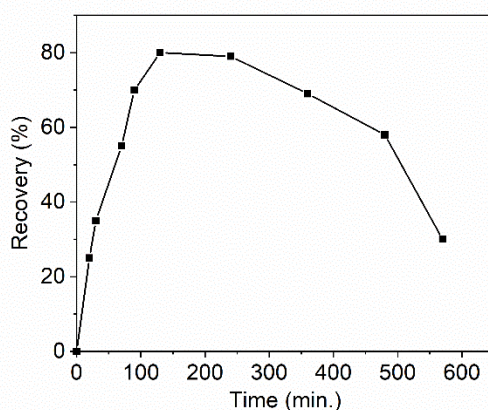


Figure 13. Effect of extraction time on the efficiency of extraction in the presence of surface active agent.

The efficiency of recovery in the step-wise method used for recovery of nickel in the presence of surface active reagents after the first and second steps with respect to effect of extraction period are presented in Figures 14 and 15.

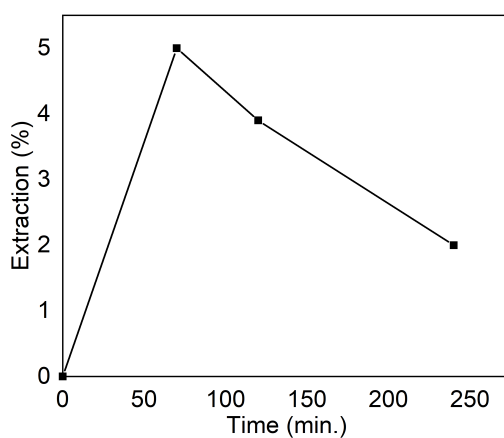


Figure 14. Effect of extraction period on efficiency of extraction for the first step.

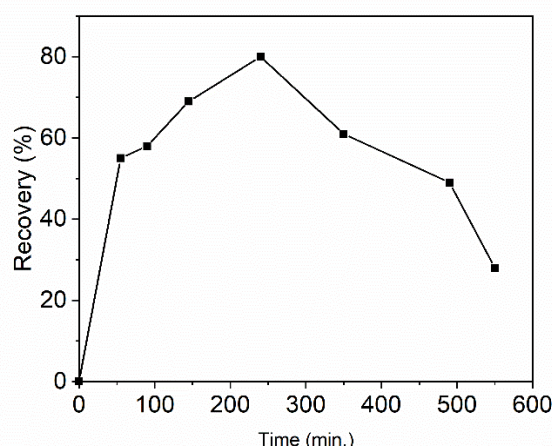


Figure 15. Effect of extraction period on efficiency of recovery.

The economic analysis of the recovery methods for the nickel catalyst, which was performed via the mathematical structure of the model is described elsewhere (Demirdogen, R.E., et al., 2005), employed seven different alternatives. The operation, the initial investment, the environmental and the replacement cost for each alternative was compared. The alternative with the least cost was chosen to be the best alternative. The results are presented in Table 6. Alternative VI, was preferred over others.

Table 6. Economic analysis results of the seven alternatives under investigation.

The Best Alternative	The Better Alternative	The Good Alternative
<u>Alternative 6</u> : employment of CCl ₄ in the presence of surface active agents with repetitive extraction and elctrolysis.	<u>Alternative 5</u> : employment of CCl ₄ in the presence of surface active agents in two steps.	<u>Alternative 7</u> : employment of CCl ₄ in the absence of surface active agents with repetitive extraction and electrolysis.

3. CONCLUSION

1) Recovering Ni catalyst via efficient and cost effective methods is of great importance since it is consumed in great amounts. The yearly nickel consumption of Turkey only through margarine is about 19.800 kg, which would mean that the yearly burden only by this industry on the economy is about 158.000 USD.

2) When production methods are to be developed the fact that production from the primary sources is neither ecological nor economical as these sources are depleting, should always be kept in mind. Moreover, the governments and the waste management policies dictate that waste recovery is of great importance. Only the wastes, which do not offer any opportunity for recovery, are to be disposed of, while the rest should be evaluated.

3) The recovery of Ni from waste catalyst can be performed by leaching out nickel via employment of (NH₄)₂SO₄ and NH₃ as extractant and pH adjustor, respectively. These reagents are by-products of various industries. However, the efficiency of the newly developed method is about 80 %. This may be due to accumulation of nickel as nickel oxides rather than as metallic Ni, while the latter remains in the solid phase. Although the efficiency may seem to be lower than that obtained in the dry method, since the demand for heat and thus energy is less and the reagents employed are by-products of other industries, the newly developed version of the wet method is both eco- and cost-efficient.

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