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Environmental Assessment of Large Scale Production of Magnetite (Fe_3O_4) Nanoparticles via Coprecipitation

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Abstract: Nanoparticles are materials with special properties that can be applied in different fields, such as medicine, engineering, food industry and cosmetics. The contributions regarding the synthesis of different types of nanoparticles have allowed researchers to determine a special group of nanoparticles with key characteristics for several applications. Magnetite nanoparticles (Fe_3O_4) have attracted a significant amount of attention due to their ability to improve the properties of polymeric materials. For this reason, the development of novel/emerging large scale processes for the synthesis of nanomaterials is a great and important challenge. In this work, an environmental assessment of the large scale production of magnetite via coprecipitation was carried out with the aim to evaluate its potential impact on the environment at a processing capacity of 806.87 t/year of magnetite nanoparticles. The assessment was performed using a computer-aided tool based on the Waste Reduction Algorithm (WAR). This method allows us to quantify the impacts generated and classify them into eight different categories. The process does not generate any negative impacts that could harm the environment. This assessment allowed us to identify the applicability of the large scale production of magnetite nanoparticles from an environmental viewpoint.

Keywords: environmental assessment; WAR algorithm; CAPE; nanoparticles

1. Introduction

The magnetic iron oxide nanoparticles are materials with important properties and can be used for different applications. The magnetite (Fe_3O_4) are a type of nanoparticles that belong to a special group and they have been drawing expressive technological interests due to their outstanding properties and potential applications in fields as medicine, biotechnology, engineering, among others [1]. Recently, nanosized magnetite particles have received major interest in the manufacturing of magnetic recording devices, protective and sensitive coatings, catalysts, pigments and ferrofluids [2]. The production of this type of nanoparticles can be carried out using different methods, such as thermal decomposition [3,4], microemulsion and coprecipitation [5]. Chemical coprecipitation is a low-cost and straightforward method for preparing semiconductor materials and it is the most common method due to its non-toxicity, the simplicity in its synthesis and its potential ability to be employed for large scale production [6].

The coprecipitation technique is widely employed for the generation of M^{2+} and Fe^{3+} cations using NaOH and NH_4OH to create alkaline conditions. The nanoparticles after the coprecipitation process are dispersed in aqueous media due to the large surface of hydroxyl groups [7]. The reaction pH value represents a key factor that controls structural morphology (e.g., crystallinity, homogeneity) and particle size of the material [8]. Tao et al. [9] reported several drawbacks in classical coprecipitation, including uncontrollability of the size, size distribution and the phase control of resultant nanoparticles. According to these authors, magnetite production has limited potential on a large scale. For these reasons, the evaluation of the coprecipitation method for synthesizing magnetite nanoparticles is important for industrial scaling-up.

The environmental assessment features an important tool for guiding the planning process and screening design alternatives [10]. Several methods have been applied to analyze the sustainability of the production systems from an environmental point of view. Life Cycle Assessment (LCA) and Waste Reduction (WAR) algorithm [11] are the most used methodologies to assess the environmental impacts of chemical processes [12]. The WAR methodology estimates potential environmental impacts (PEI) of any chemical process, based on atmospheric and toxicological categories [13]. Some literature contributions have focused on the environmental assessment of emerging and novel chemical processes. Cassiani-Cassiani et al. [14] performed an environmental evaluation of agar production from the macroalgae feedstock *Gracilaria* sp. and reported that the value of PEI generated was around 118 PEI/h. Meramo et al. [15] studied the synthesis of titanium dioxide (TiO_2) nanoparticles from titanium isopropoxide (TTIP) via green chemistry and quantified how this process meets sustainability standards through the WAR algorithm.

In this work, an environmental evaluation is developed for a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation with the aim of determining the degree of pollution generated by the process. The WAR algorithm was selected for the environmental analysis of the mentioned process through computer-aided process engineering using the WARGUI software. The novelty of this research is the modeling, simulation and scaling-up of magnetite nanoparticles synthesis process previously performed by authors at a lab scale.

2. Materials and Methods

2.1. Process Description

The large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation consists of several stages, as shown in Figure 1. The iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and iron (III) chloride hexahydrate ($FeCl_3$ $6H_2O$) solutions are fed into the process in a 1:2 ratio and they are subsequently mixed in a first stage. The resulting mixture (stream 3) is sent to a reactor where sodium hydroxide solution (NaOH) is added, which acts as a precipitating agent and allows the execution of the reaction. This ultimately forms the magnetite nanoparticles. The resulting stream (stream 5) is cooled before being sent to a centrifuge in which the objective is to separate the nanoparticles formed from the rest of the components present in the stream. After this, stream 8 is sent to a washing unit with water and ethanol where sodium hydroxide, water and sodium chloride are removed and finally, the nanoparticles are dried.

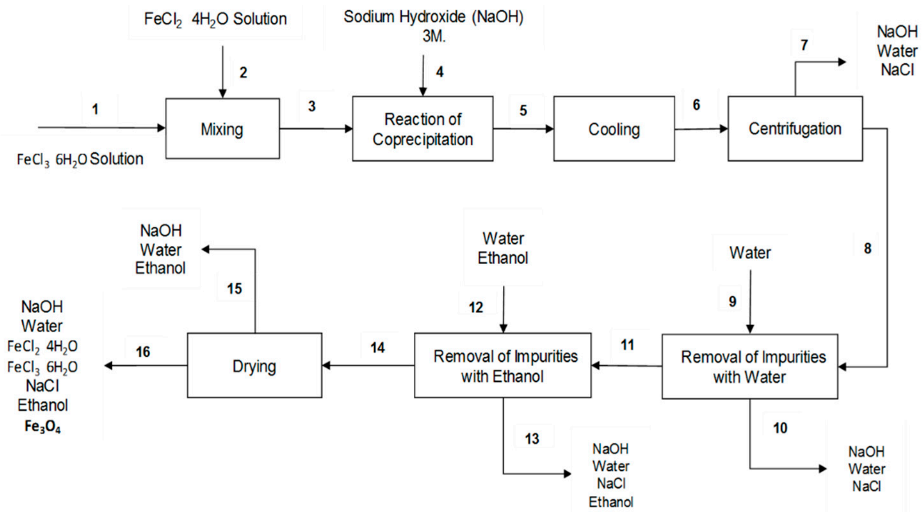

Figure 1. Block diagram of a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation.

2.2. Environmental Assessment Using the Waste Reduction Algorithm (WAR)

For the environmental assessment of a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation, the waste reduction algorithm (WAR) was selected using the WARGUI software. This tool allows us to quantify the potential environmental impact from the generation of the products of the activities of the chemical industry and it has the capacity to indicate how fast an environmental impact from the process might possibly occur. This quantification of the output and/or generation rate of Potential Environmental Impacts (PEIs) cannot be performed using other methodologies as the Life Cycle Assessment (LCA) in its basic structure [16]. The waste reduction algorithm introduces the concept of Potential Environmental Impact (PEI) and evaluates it in eight different impact categories that are divided into two major groups: toxicological and atmospheric impacts [13].

2.2.1. Toxicological Impact Categories

Human Toxicity Potential by Ingestion (HTPI), which can be calculated for a chemical if it exists as a liquid or a solid at the temperature of 0 °C and atmospheric pressure [17], is defined according to Equation (1).

$$HPTI = \frac{1}{LD_{50}} \tag{1}$$

where LD_{50} (mg chemical/kg rat) is the lethal dose that produced death in 50% of rats after oral ingestion. This measure has been frequently used in the literature and is widely accepted as a standard toxicity indicator. Human Toxicity Potential by Inhalation Dermal Exposure (HTPE) is determined for a chemical if it exists as a gas at the temperature of 273 K and 1 atm [17]. To estimate the HTPE, the time-weighted averages (8 h) of the threshold limit values (TLV) are used according OSHA, ACGIH and NIOSH.

$$HTPE = \frac{1}{TLV} \tag{2}$$

Aquatic Toxicity Potential (ATP) is determined using the toxicological data for a representative species of fish (*Pimephales promelas*) [17]. This species was chosen because it is accepted as an universal aquatic indicator and there are reported data concerning this species.

$$ATP = \frac{1}{LC_{50}} \tag{3}$$

where LC_{50} is the lethal concentration, which causes death in 50% of the test specimens after oral ingestion. Terrestrial Toxicity Potential (TTP) is determined using the rat-oral LD_{50} according to Equation (4).

$$TTP = \frac{1}{LD_{50}} \tag{4}$$

2.2.2. Atmospheric Impact Categories

Global Warning Potential (GWP) is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent that CO_2 absorbs infrared radiation over its respective lifetimes [17]:

$$GWP = \frac{\int_0^t a_i c_i(t)dt}{\int_0^t a_{CO_2} c_{CO_2}(t)dt} m_i \tag{5}$$

where a_i and a_{CO_2} are the radiation heat absorption per unit of greenhouse gas i and per unit of carbon dioxide; $c_i(t)$ and $c_{CO_2}(t)$ is the greenhouse gas i concentration and the carbon dioxide concentration in a time t after being released; t is the number of years over which GWP will be evaluated; and m_i is the mass (kg) of the emitted gas. Ozone Depletion Potential (ODP) is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen [17]:

$$ODP = \frac{\delta[O_3]_i}{\delta[O_3]FCKW-11} m_i \tag{6}$$

where $\delta[O_3]_i$ and $\delta[O_3]FCKW-11$ refers to the depletion of global ozone produced by a gas i and CFC-11 unit; and m_i is the mass (kg) of the emitted gas. Photochemical Oxidation Potential (PCOP) is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical (OH-) to the rate at which a unit mass of ethylene reacts with OH- [17]:

$$PCOP = \frac{\frac{a_i}{b_i(t)}}{\frac{a_{C_2H_4}}{b_{C_2H_4}(t)}} m_i \tag{7}$$

where a_i and $a_{C_2H_4}$ is the change in ozone concentration due to the change in a volatile organic compound emission and due to the change in ethylene emission; $b_i(t)$ and $b_{C_2H_4}(t)$ is the integrated emission of a volatile organic compound i up to a time t and the integrated emission of ethylene at the same time; and m_i is the mass (kg) of the emitted gas. Acidification Potential (AP) is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2 [17]:

$$AP = \frac{\frac{V_i}{M_i}}{\frac{V_{SO_2}}{M_{SO_2}}} m_i \tag{8}$$

where V_i and V_{SO_2} are the acidification potential of component i and SO_2; M_i and M_{SO_2} is the mass unit of substance i and SO_2; and m_i is the mass (kg) of the emitted substance i. The WAR algorithm relates the PEI to the flow of an environmental impact across the boundaries of the system as a consequence of the mass and energy that crosses these limits. This algorithm handles two types of indices to assess the environmental impact of a chemical industry. The first class measures the PEI emitted by the process and the other class measures the PEI generated. Within each class, two indices are defined: total output impact indices expressed as the impact potential per unit of time and impact indices per product mass. The main objective of the PEI output is to assess the external environmental efficiency of the process, that is, the capacity of the process to obtain final products at a minimum discharge potential. Regarding the PEI generated, the most important thing is to know the internal environmental efficiency of the process. The total output rate of PEI is calculated using Equation (9); the total mass output rate is calculated by Equation (10); the total generation rate is calculated by Equation (11); and the total mass generation rate is calculated using Equation (12).

$$i_{out}^{(t)} = i_{out}^{(cp)} + i_{out}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)} = \sum_{j}^{cp} M_j^{(out)} \sum_{k}^{cp} X_{kj}\psi_k + \sum_{j}^{ep-g} M_j^{(out)} \sum_{k}^{ep-g} X_{kj}\psi_k \quad (9)$$

$$i_{out}^{(t)} = \frac{\left(i_{out}^{(cp)} + i_{out}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)}\right)}{\sum_P P_P} = \frac{\sum_j^{cp} M_j^{(out)} \sum_k^{cp} X_{kj}\psi_k + \sum_j^{ep-g} M_j^{(out)} \sum_k^{ep-g} X_{kj}\psi_k}{\sum_P P_P} \quad (10)$$

$$\begin{aligned} i_{gen}^{(t)} &= i_{out}^{(cp)} - i_{in}^{(cp)} + i_{out}^{(ep)} - i_{in}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)} \\ &= \sum_{j}^{cp} M_j^{(out)} \sum_{k}^{cp} X_{kj}\psi_k - \sum_{j}^{cp} M_j^{(in)} \sum_{k}^{cp} X_{kj}\psi_k + \sum_{j}^{ep-g} M_j^{(out)} \sum_{k}^{ep-g} X_{kj}\psi_k \end{aligned} \quad (11)$$

$$\begin{aligned} i_{gen}^{(t)} &= \frac{\left(i_{out}^{(cp)} - i_{in}^{(cp)} + i_{out}^{(ep)} - i_{in}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)}\right)}{\sum_P P_P} \\ &= \frac{\left(\sum_j^{cp} M_j^{(out)} \sum_k^{cp} X_{kj}\psi_k - \sum_j^{cp} M_j^{(in)} \sum_k^{cp} X_{kj}\psi_k + \sum_j^{ep-g} M_j^{(out)} \sum_k^{ep-g} X_{kj}\psi_k\right)}{\sum_P P_P} \end{aligned} \quad (12)$$

where $i_{out}{}^{(cp)}$ and $i_{in}{}^{(cp)}$ are the rate of PEIs out and into of the system due to chemical interactions within the system, respectively; $i_{out}{}^{(ep)}$ and $i_{in}{}^{(ep)}$ are the rates of PEI out and into the system due to energy generation processes within the system; and $i_{we}{}^{(ep)}$ and $i_{we}{}^{(cp)}$ are the PEIs out of a system as a result of the release of waste energy due to energy generation and chemical processes within the system. Furthermore, $M_j{}^{(in)}$ and $M_j{}^{(out)}$ are the input and output mass flow rates of stream j; X_k is the mass fraction of a component k in the stream j; ψ_k is the overall Potential Environmental Impact of chemical k; and P_p is the mass flowrate of product p [18].

To perform the environmental evaluation of a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation, four study cases were formulated. Case 1 is proposed without considering the energy and product streams. Case 2 considers the environmental impacts of the product streams without energy contribution. On the other hand, Case 3 considers the environmental impacts of the energy sources without product stream contribution and Case 4 considers the contribution of both energy and product streams to the potential environmental impacts. The combination of global impact analysis, impacts by category, effect of energy flow and source of energy allowed us to obtain a good diagnosis of the environmental viability of the process.

3. Results and Discussion

3.1. Total Potential Environmental Impact (PEI)

Figure 2 shows the results corresponding to the total PEI generated and total PEI output per kilogram of product and per hour for all cases. We can observe that the total PEIs generated for each case were negative (-7.35×10^2, -7.12×10^2, -7.10×10^2, -6.87×10^2 PEI/h), which indicates that the process is environmentally friendly. It can be observed that for all cases, the total PEI output per kilogram of product is an insignificant value while in the base case (case 1), the total PEI output value per hour is lower than the other cases. Thus, it is evident that the energy and the products contribute to a small increase in the total PEI output. On the other hand, for the case in which the product and energy are included (case 2) and (case 3), the PEI output values are equal. These results indicate that the inclusion of the product stream or energy generate the same impacts and contributes to an increase in the total PEI output.

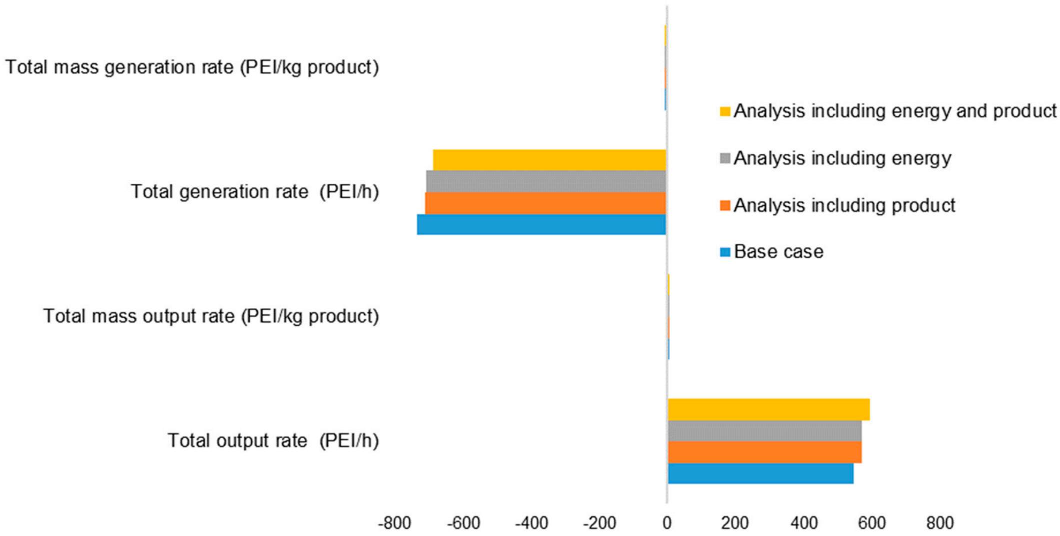

Figure 2. Total PEI generated and output of large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation.

3.2. Local Toxicological Impacts

Figure 3 shows the local toxicological impacts generated and the output of the process, which includes human (HTPI and HTPE) and ecological (ATP and TTP) impacts for all cases. There is evidence that the output and generated impacts for the ATP category are insignificant in the four cases studied. This indicates that the impacts generated by this process on aquatic systems and the mass flow that is expelled into the atmosphere are low as the output HTPI and TTP values are equal in each cases (4.8 PEI/h, 5.83 PEI/h, 4.86 PEI/h and 5.88 PEI/h, respectively). These results indicate that the inclusion of the product stream and energy causes a slight increase in HTPI and TTP categories. Furthermore, there is a minimum value for PEIs generated in the four impact categories. This suggests that the processes have less toxic chemical substances in the product streams, which also have tolerance values limits (TVL) that are lower than those fed into the system.

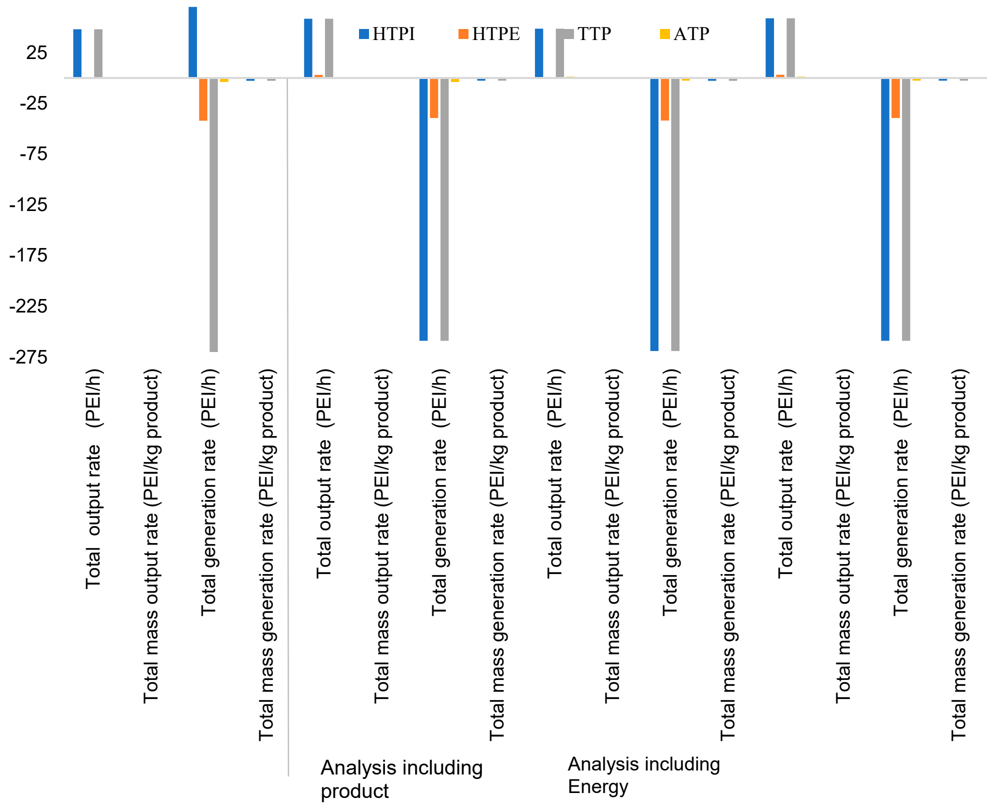

Figure 3. Local output and generated toxicological impacts of large-scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation.

3.3. Atmospheric Impacts

Figure 4 shows the atmospheric global (GWP and ODP) and regional (PCOP and AP) impacts for all cases. We observed that the values for GWP and ODP are insignificant in all cases, which leads to the conclusion that the process is neutral under these categories and the use of fuels as an energy source does not contribute to the production of PEI in these categories. For cases 3 and 4, the PEI output for AP are (2.13×10^1 PEI/h) while this is zero for the other cases. Thus, the required energy in the process contributes to the generation of acid rain while the PEI output for PCOP category is equal for all cases (4.50×10^2 PEI/h). On the other hand, the process does not generate atmospheric impacts in the GWP, ODP and PCOP categories while the use of fuels generates impacts related to the AP category.

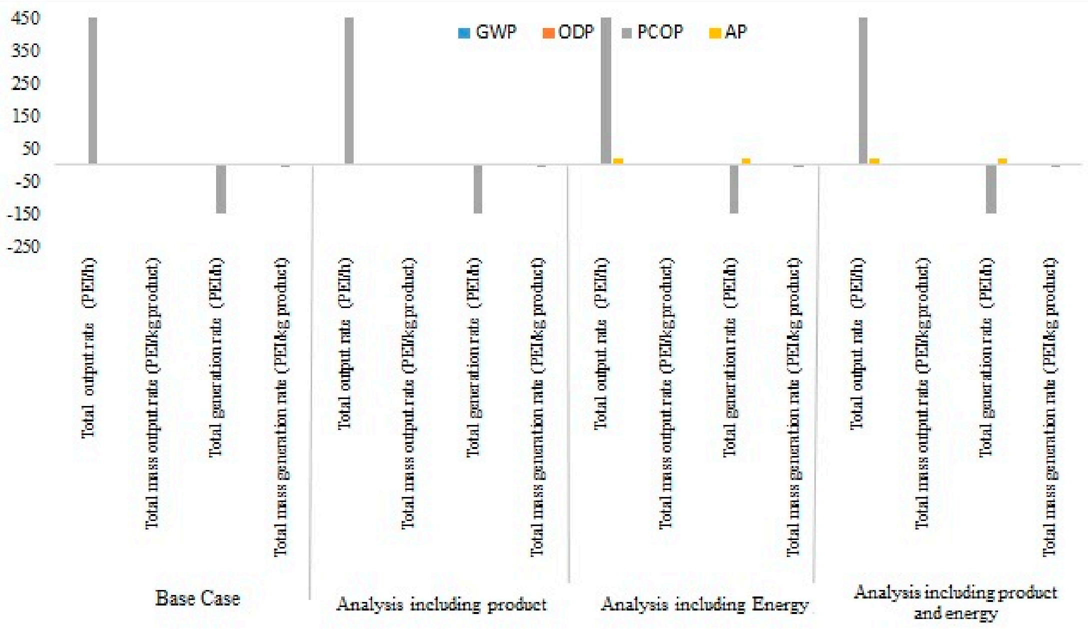

Figure 4. Output and generated atmospheric impacts of the process of a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation.

3.4. Effect of Energy Source

Three types of fuel (gas, coal and oil) were analyzed for the evaluation of the potential impact for the eight categories. Figure 5 shows the changes in the PEI output for each category and for the different fuels used in the large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation. It can be initially observed that the PEI outputs are low for each category, except for the AP category. However, it can be determined that the use of coal increases the impact in each category, especially in the AP category (3.4×10^1) because the coal releases more hydrogen ions than reacting with SO_2, causing acid rains [19]. Additionally, it can be evidenced that the use of the gas as the fuel for this process generates the smallest impacts in each category.

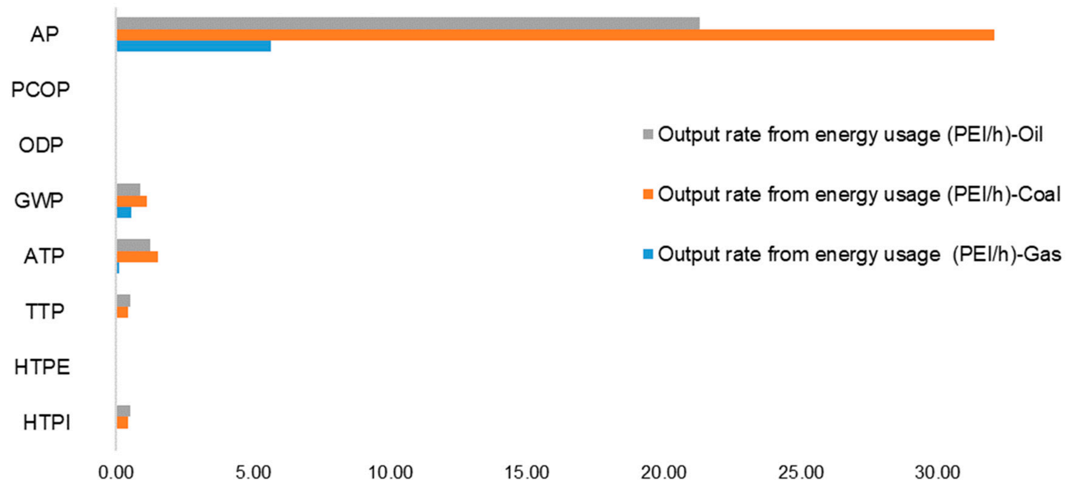

Figure 5. Effect of energy source on output rate from energy usage of the process of a large scale production of magnetite (Fe_3O_4) nanoparticles via coprecipitation.

4. Conclusions

The waste reduction algorithm (WAR) was implemented for the environmental assessment of the large scale production of magnetite (Fe_3O_4) via coprecipitation. From the results obtained, it can be established that the process is not harmful to the environment as the process transforms the feed streams with high PEI into final products with lower PEI. This is reflected in the total PEI generated, which were negative values in all cases. It was also determined that the major sources of potential environmental impacts were found in stream 7 that originated from the centrifugation unit. On the other hand, there is evidence from the toxicological impact assessment that the process did not generate impacts on aquatic systems. Furthermore, the environmental impacts for the other toxicological categories (HTPI, HTPI and TTP) were not significantly high, which indicate that the product synthesized in this process contains fewer toxic chemicals than those contained by the process feeding. This is a positive finding from an environmental viewpoint. In addition, the performance of the atmospheric categories showed that this process is neutral in the evaluated parameters, except for the AP category as using this type of fuel as an energy supply could contribute to the generation of acid rain effects. Using coal as the fuel for an energy supply increases the environmental impacts for this process. Furthermore, it was determined that the most convenient fuel from the evaluated options is natural gas. Therefore, it can be concluded that the large scale production of magnetite nanoparticles via coprecipitation is respectful of the environment according to the performance obtained from the application of WAR GUI software to this case study.

Author Contributions: S.J.A.-D., S.I.M.-H., J.L.-P., A.Z. and A.D.G.-D. conceived and designed the paper. S.J.A.-D. and S.I.M.-H. wrote the Introduction and Materials and Methods. S.I.M.-H., S.J.A.-D. and A.D.G.-D. wrote the Results and prepared figures and tables. Discussions and Conclusions were the collective work of all authors. The writing-review & editing was performed by A.D.G.-D., J.L.-P. and A.Z. A.D.G.-D. supervised the development of this paper.

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