CHEMICAL ENGINEERING TRANSACTIONS
VOL. 70, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216
DOI: 10.3303/CET1870178

Environmental Assessment of a Large-Scale Production of TiO_2 Nanoparticles via Green Chemistry

Samir I. Meramo[a,c], Heidy Bonfante[b], Gesira De Avila-Montiel[b], Adriana Herrera-Barros[a], Angel Gonzalez-Delgado[a,*]

[a]Nanomaterials andComputer Aided Process Engineering Research Group (NIPAC), Chemical Engineering Department Faculty of Engineering, University of Cartagena, Av. del Consulado Calle 30 No. 48-152, Cartagena, Colombia.
[b]Process Design and Biomass Utilization Research Group (IDAB), Chemical Engineering Department, Faculty of Engineering, University of Cartagena, Av. del Consulado Calle 30 No. 48-152, Cartagena, Colombia
[c]Engineering PhD. Program, University of Cartagena, Av. del Consulado Calle 30 No. 48-152, Cartagena, Colombia
agonzalezd1@unicartagena.edu.co

Green chemistry concept is currently implemented in order to stimulate the development of sustainability processes and pollution prevention. However, not for all cases the use of this type of process generates an operation with good environmental performance, also in the development and evaluation of new topologies, such as the one presented in this paper, environmental assessment becomes in an important tool in order to optimize the process. In this work for developed a synthesis of titanium dioxide (TiO_2) nanoparticles from titanium isopropoxide (TTIP) via green chemistry. Environmental assessment was performed using software WAR GUI, which use Waste Reduction Algorithm in order to quantify potential environmental impacts generation and output environmental impacts for this process for 4 different cases. Results show that the process doesn't generate high potential environmental impacts (PEI) with a rate of $1.43X10^2$ PEI/h for the case that include energy and product contributions, which represents a very low value compared to the total output rate for this case ($1.21X10^4$ PEI/h). For toxicological categories, it was obtained that for human toxicity by ingestion (HTPI) and terrestrial toxicity potential (TTP) categories exist some environmental impacts due to presence of TTIP in a high concentration, additionally these effects are increased by propanol, as a subproduct of the hydrolysis, and ethanol as solvent for the purification stage. For the aquatic matrix the potential impacts obtained was relatively low. On the other hand, it was determined for atmospheric effects that the presence of the alcohols in the process rises the potential impact related to the photochemical oxidation potential category.

1. Introduction

Green Chemistry is related to a new idea which is developed in the industry and research context as a natural evolution of pollution prevention strategic. The use of this kind of process brings the concept of developing chemical plants that can reduce waste and demand on diminishing resources. In Green Chemistry it can employ processes that use smaller amounts of energy maintaining economic growth and opportunities while providing reasonably priced products and services to a growing world population (Hendershot, 2015).
Nanotechnology is a revolutionary science related to manipulate substances at atomic or molecular scale, and its ability to work that scale. Research areas are related to the needed of developing large scale pathways for production of nanomaterials, the main products in this type of processes. Recently, metal oxide nanoparticles have attracted attention by their potential application in different fields, especially TiO_2 nanoparticles are very important due to its uses as pollution remover, photo-catalyst, virus sterilizer, among others (Wang et al., 2016).
The environmental assessment is an important tool in design and analysis of processes because its develop is useful to identify improvement areas from environmental point of view, serving as an instrument for making decision and quantification of environment impacts due to random discharge to the environment of raw material, chemicals, products, wastes or any of the substances involved in the operation in the evaluated process (Herrera et. al., 2017).

Please cite this article as: Meramo S.I., Bonfante-Alvarez H., Avila-Montiel G.D., Herrera-Barros A., Gonzalez-Delgado A.D., 2018, Environmental assessment of a large-scale production of tio2 nanoparticles via green chemistry , Chemical Engineering Transactions, 70, 1063-1068 DOI:10.3303/CET1870178

In this work, a green synthesis of TiO_2 nanoparticles was analyzed using WAR algorithm to evaluate eight impact categories, which are: human toxicity by ingestion (HTPI), human toxicity by dermal exposure or inhalation (HTPE), aquatic toxicity potential (ATP), terrestrial toxicity potential (TTP), global warming (GWP), ozone depletion (ODP), photochemical oxidation potential (PCOP) and acidification potential (AP) (Ramirez-Cando et al., 2017). In this work the research gap is addressed in order to develop an environmental assessment for a novel-proposed large-scale production of TiO_2 nanoparticles for its potential use in water treatment, photo-catalyst systems, among others. This synthesis was analyzed using computer-aided process engineering, this is related to the fact that there is no bibliography reported for the industrial scale-up, simulation and environmental evaluation of this type of process. The plant was simulated in a commercial process simulation software, having as main raw materials leaves of lemongrass and diluted titanium isopropoxide. The mass and energy balances obtained from the simulations were used in WAR algorithm to develop the environmental assessment, which will allow to determine the environmental benefits related to the process, as well as establish comparisons according to the most impacted categories and the differences in the use of different sources of energy as oil, carbon or gas (Ming Kwee et al., 2017).

2. Methods

2.1. Process description

The process was simulated for a production capacity of 5,724.16 t/y of TiO_2 nanoparticles, this amount of product was aimed due to the requirement of lemon grass for the process, which is 32,588.21 t/y, and this value was set as approximately the 30 % of total lemon grass availability in Colombia. The green synthesis of this material implies the use of titanium isopropoxide (TTIP) as precursor using lemon grass extract (lemon grass oil) as surfactant to guarantee the nano-size of particles. The Figure 1 shows the process diagram for simulated case.

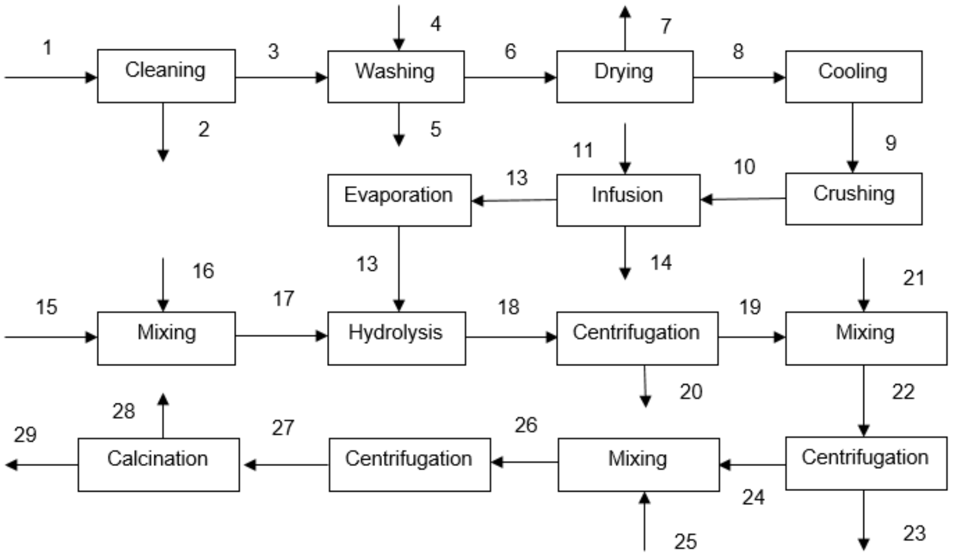

Figure 1. Process Diagram for TiO_2 green chemistry production

The production of TiO_2 nanoparticles via green chemistry, it can be estimated as an ecological synthesis because the lemon grass extract (oil) is used as a solvent for the nanomaterial production, which is developed from TTIP hydrolysis, this reaction is shown in the Eq(1) (Buerguer et al., 2015).

$$Ti(OC_3H_7)_4 + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH \quad (1)$$

The process starts with lemon grass oil extraction. For this stage, the lemon grass is cleaned, and cellulosic material is removed and sent to drying. The stream outs at a high temperature, thus the lemon grass is cooled to environmental temperature (28 °C). Next the flow is sent to crushing for reducing particle size, this is necessary to produce the infusion what allows the liquid extraction of oil. Ranitha et al. (2014) mentioned in their work that the lemon grass oil mainly contents myrcene, neral, geranial, citral, nerol, among other, with a total composition of oil of 1.10 % w/w. For the extraction stage a lot of water is used so it is necessary to implement an evaporation stage in order to reduce moisture content. For this stage was extract 7,284.31 t/y phytochemicals with an oil content of 4.2 %.

On the other hand, the main flow of raw material (TTIP) is sent to a mixing tank to make a quickly mixing with water. The TiO_2 is formed from hydrolysis reaction of TTIP with H_2O, but to guarantee the nano-particle size is necessary to introduce the phytochemicals (lemon grass oil) before the reaction, for lab scale was obtained a yield of 0.93 mol of TTIP per mol of TiO_2. Propanol is generated as byproduct of the reaction and it´s necessary to extract this compound to avoid possible contamination of the nanomaterial. The outlet stream of the reaction with a high content of water and nanoparticles in suspension, is sent to a train of purification, to perform the purity of TiO_2, based in a centrifugation and mixing process scheme. For centrifuges units 1 and 3, removal water is used, for unit 2 ethanol (70 % v/v) is involved in the purification. Finally, the main outlet stream is sent to a furnace for drying the particles and it is cooled to the environment temperature.

2.2. Environmental assessment

Waste Reduction Algorithm (WAR) methodology was chosen to develop the environmental analysis using WAR GUI Software, this tool was selected taking into account the open availability of the software and its ability to quantify the rate of potential environmental impacts (PEI) generation (or consumption) for processes taking into account energy streams and products (Meramo et al., 2018). The process was analyzed through different points of view, varying the energy source (gas, oil and coal), energy contribution and product PEI generation. A case 1 is based without contributions of energy sources and product stream, case 2 considered product in the PEI balance, case 3 counts energy source without products and case 4 considered all variables (process, products and energy contributions). The WAR evaluated the environmental performance through 8 different impact categories, toxicologically: HTPI, HTPE, ATP and TTP, atmospherically: GWP, ODP, PCOP and AP (Ramirez-Cando et. al., 2017). The assessment was developed through four criteria, the first was in order to developed of the global evaluation for total mass output and generation rate of PEI, the second and third were based in the toxicologically and atmospherically effects, respectively. The last approach was based for the analysis of three different energy sources (oil, gas and coal) and its contribution for the total mass output rate, with the aim of determine which of the energy sources have the best environmental performance and compare if it is environmentally favorable the use of the residual cellulose (assumed as coal) as source for cogeneration system or use another energy supply (Hernandez et al., 2013).

3. Results and discussion

3.1. Total PEI: generation and output

From Figure 2, the PEI generated were a positive but relatively low values for all 4 cases (7.64 x 10^1, 9.26 x 10^2, 1.26 x 10^2 and 1.43 x 10^2 PEI/h), which indicates that the operation has a good environmental performance with a generation of potential impacts not significantly high.

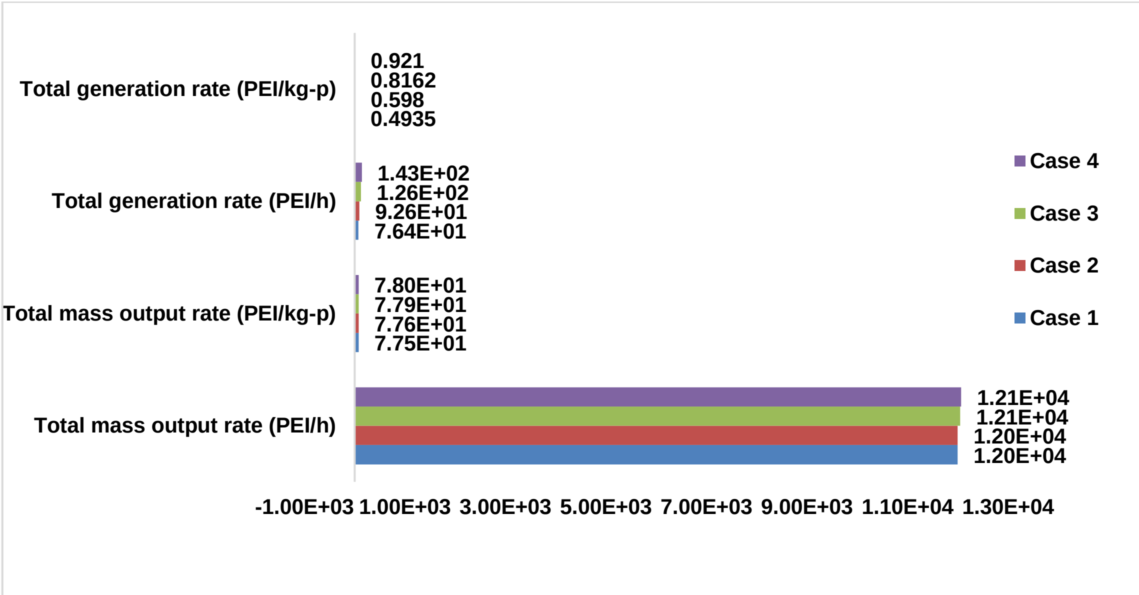

Figure 2. Total PEI generated and output of the system for TiO_2 nanoparticles large scale production.

Regarding PEI output, it can be observed PEI output per kilogram of product and PEI output per hour are in a similar proportion, which shows that the influence obtained by energy and products inclusion does not generate general environmental impacts.

3.2. Toxicological impacts: Generated and Total mass output rates

Figure 3 shows the toxicological impacts generated and output of the process. It observed that the output impacts directed HTPI and HTPE are more significant for all scenarios compared to the ecological output impacts (TTP and ATP).

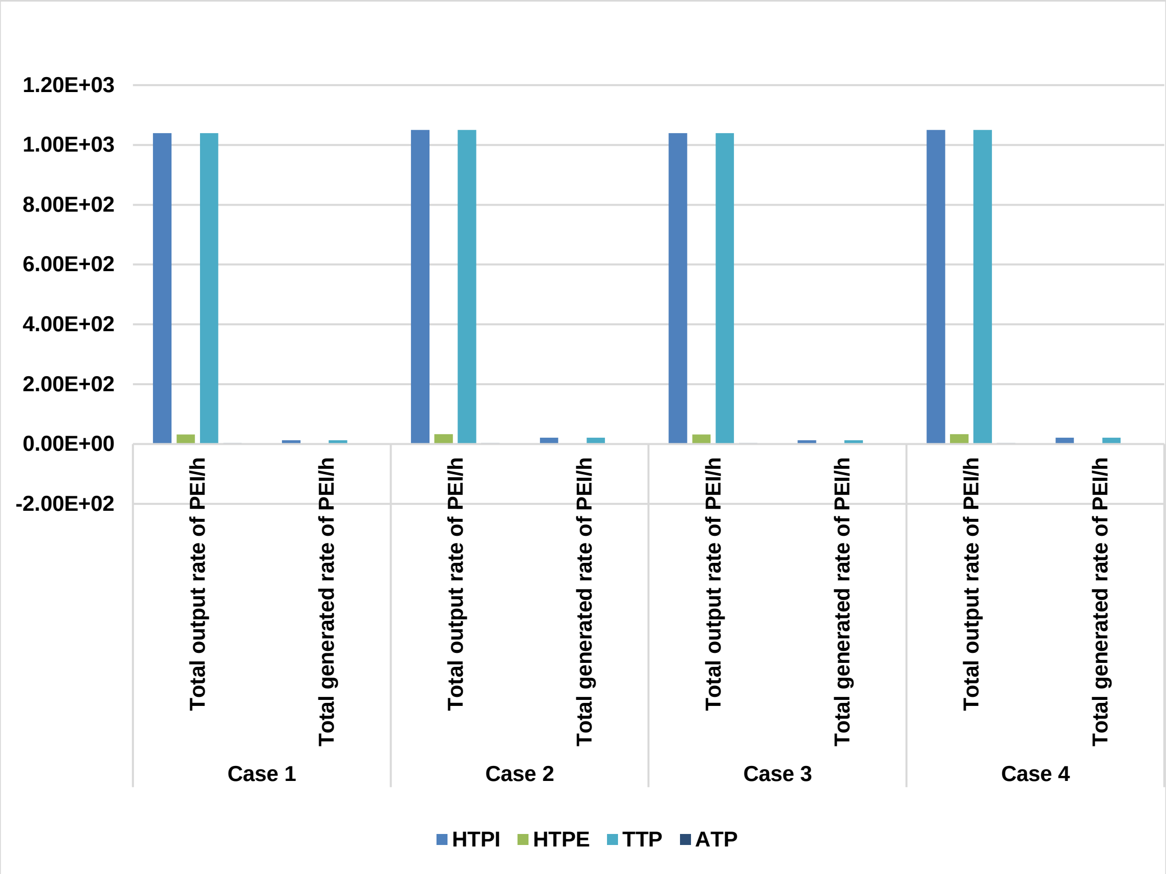

Figure 3. Total mass output and total generated rate for toxicologically effects

3.3. Atmospherically impacts: Generated and Total mass output rates

Figure 4 shows that atmospheric impacts are composed for four impacts categories related to the global effects (GWP y ODP) and regional (AP y PCOP) ones. In general, the toxicologically values for PEI output under ATP impact category are considerably lower (2.75 PEI/h for cases 1 and 2; and 3.49 PEI/h for cases 3 and 4) compared to TTP and HTPI (1.04×10^3 PEI/h for cases 1 and 3, and 1.05×10^3 for cases 2 and 4), so that the impacts generated by this process on aquatic systems are low. In general, the PEI generated for HTPI and TTP impact categories was moderately significant, so it can be inferred that the process has both in the inlet stream and in the outlet waste and products toxic chemicals with which care must be taken for possible random discharges to the environment.

The result of the analysis shows that for ODP and AP categories in cases 1 and 2 are zero, which leads to the conclusion that this process is environmentally neutral under these categories, so the contribution to PEI output for atmospheric categories comes from the use of fuels in the process as energy sources, as occurs in cases 3 and 4. The PEI output for GWP (1.93×10^1 PEI/h) and AP (1.60×10^2 PEI/h) impact categories in cases 3 and 4, indicates that this process emits chemicals that persist longer in the environment due to its low oxidation and also can contribute to the generation of acid rain. The fact that the PEI generated, and PEI output values are very similar owing to chemical products obtained presents reduced ability to degrade themselves in the environment.

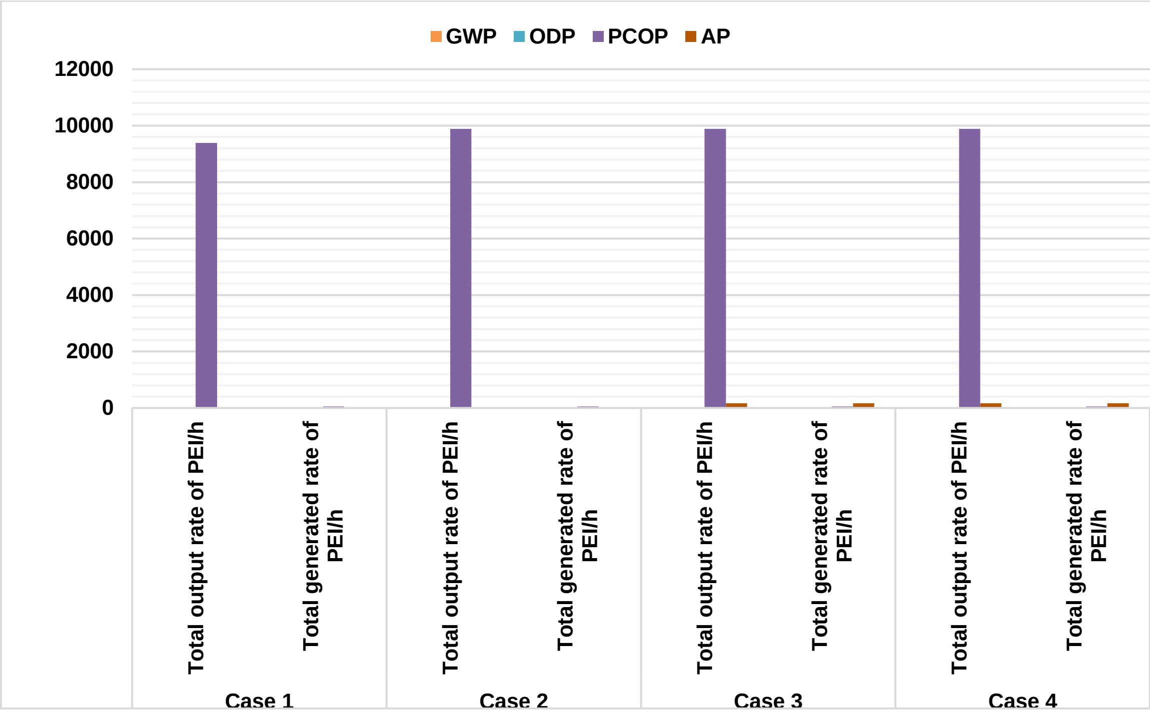

Figure 4. Total mass output and generated rate for atmospherically effects

3.4. Energy source analysis

For this approach, the contribution of three different types of fuel (gas, coal and oil) for each impact category was evaluated, including the energy consumption of process and excluding the product stream. Figure 5 shows the comparison of the energy source in PEI total mass output rate based for TiO_2 green chemistry production process.

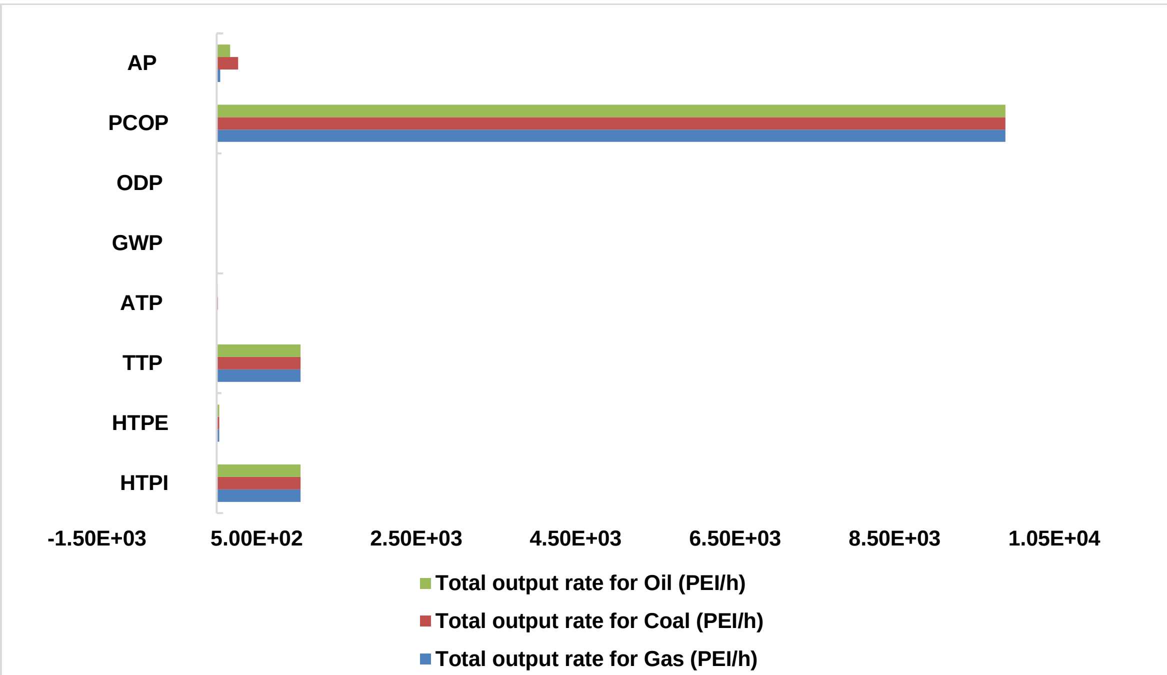

Figure 5. Energy source approach on output rate for TiO_2 nanoparticles production

It was obtained that coal usage increases the impact in the AP ($2.70x10^2$ PEI/h), for the other impacts categories it wasn´t obtained important differences in the PEI values. Compared to the global output rate of PEI for the process, the potential environmental impacts from energy source they do not represent many concerns because its contribution is less compared to other effects previously described, so this process has a good energetic performance from an environmental point of view. It can be observed that gas had a better performance compared to the others energy sources.

4. Conclusions

Waste Reduction Algorithm was implemented for environmental assessment of a green synthesis of large scale TiO_2 nanoparticles. From results obtained, it can be suggested that the process needs improvements focused in the potential impacts because for this operation exits some concerns about toxicology and atmospheric potential impacts due to the substance implies in the process, which is reflected in important amount for total output PEI for all cases studied. Specifically, for toxicologically effects it was obtained that the most impacted categories were HTPI and TTP, this is related to the impacts due to use ethanol as a solvent, and propanol is formed in the hydrolysis reaction, additionally to the handle of TTIP as a main raw material. The organics alcohols also had effects in the atmospherically categories, with PCOP category with the most PEI output, thus some strategy to increase the environmental performance of the process, it can be replacing ethanol as solvent for other substances that have less environmental potential impacts.

Acknowledgments

The authors thank to the Colombian Administrative Department of Science, Technology and Innovation COLCIENCIAS for the financial support of the project “Removal of polycyclic aromatic hydrocarbons (PAHs), present in coastal waters Cartagena bay by using shrimp exoskeleton as a source of nanoparticle-modified bioadsorbents”, code 1107748593351 CT069/17. Thanks to the Engineering Ph.D. Program and the Research Vice-rectory of the University of Cartagena for its support of this publication within the framework of the Plan for Strengthening the Doctoral Program in Engineering 2017-2018.

References

Buerguer P., Nurkowski D., Akroyd J., and Kraft M., 2015, A kinetic mechanism for the thermal decomposition of titanium tetraisopropoxide New Museums Site, Preprint, Cambridge Centre for Computational Chemical Engineering, DOI: 10.1016/j.proci.2016.08.062

Carvajal J.C., Gomez A., and Cardona, C., 2016, Comparison of lignin extraction processes: Economic and Environmental assessment, Bioresource Technology, 214, 468-476.

Hendershot, D., 2015, Green Chemistry and Process Safety, Journal of Chemical Health and Safety, 22, 39. DOI: 10.1016/j.jchas.2015.10.010.

Hernandez V., Romero J., Davila J., Castro E., and Cardona C., 2013, Techno-economic and environmental assessment of an olive stone based biorefinery, Resources, Conservation and Recycling, 92, 145-150.

Herrera R., Salgado J., Peralta Y., and González A., 2017, Environmental Evaluation of a Palm-based biorefinery under North-Colombian Conditions. Chemical Engineering Transactions, 57, 193-198. DOI: 10.3303/CET1757033.

Lee M.K., Hashim H., Ho C.S., Ho W.S., Lim J.S., 2017, Economic and Environmental Assessment for Integrated Biogas Upgrading with CO_2 Utilization in Palm Oil Mill, Chemical Engineering Transactions, 56, 715-720. DOI: 10.3303/CET1756120.

Meramo S., Ojeda K., and Sánchez E., 2018, Environmental assessment of a biorefinery: Case study of a purification stage in biomass gasification, Contemporary Engineering Sciences, 11 (3), 113-120.

Ramirez-Cando L., Spugnoli P., Matteo R., Bagatta M., Tavarini S., Foschi L., and Lazzeri L., 2017, Environmental Assessment of Flax Straw Production for NonWood Pulp Mills, Chemical Engineering Transactions, 58, 787-792.

Ranitha M., Abdurahman H., Sulaiman Z., Nour, Z., Nour A., and Thana Raja S., 2014, A Comparative Study of Lemongrass (Cymbopogon Citratus) Essential Oil Extracted by Microwave-Assisted Hydrodistillation (MAHD) and Conventional Hydrodistillation (HD) Method, International Journal of Chemical Engineering and Applications, 5, 104-108, DOI: 10.7763/IJCEA.2014.V5.360.

Wang P., Lombi E., Zhao F., and Kopittke P., 2016, Nanotechnology: A New Opportunity in Plant Sciences, Trends in Plant Science, 21, 699-712, DOI: 10.1016/j.tplants.2016.04.005