Analysis of the environmental impact using the Waste Reduction Algorithm WAR in polypropylene process production by applying grade Transitions strategies

Alexis Velásquez-Barrios[1,2], Cesar Rueda-Duran[1,2], Enrique Mogollón[1], Juan Carlos Alvarez[1], Rodney Cardona[1], Carlos Ariel Cardona-Alzate[2*]

[1]Grupo de Investigación en Tecnología de Polimeros, Esenttia (Polipropileno del Caribe S.A.), Zona Industrial de Mamonal Km 8, A.A. 4336, Cartagena, Colombia.

[2]Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia sede Manizales, Manizales, Colombia

*Corresponding author: ccardonaal@unal.edu.co
Tel.: +57 6 8879300x50417; Fax: +57 6 8879300x50452.

Keywords: *Polymerization process, Grade Transitions, Environmental Impact.*

Abstract

In any kind of process production, the most important challenge consists in minimizing environmental impacts while maintaining market competitiveness. The use of environmental practices is an excellent way to achieve these goals. Among the alternatives are the Cleaner Production methodologies that integrate technological, economic and environmental strategies into processes or products to increase the efficiency of input and raw material usage by reducing waste, minimizing or recycling generated waste, and providing economic and environmental benefits for organizations[1]. Nowadays the global industrialization, the population growth, and the high production and excessive consumption contributed to the economic development, but resulted in environmental degradation of the ecosystems. In this context, the development of corporate environmentalism, as a strategic part of business, is one of the most significant changes that began to occur in the markets at the beginning of the XXI century.[2].

In the petrochemical industry, specifically in the production process of polypropylene, more than 60 types or grades of polypropylene are produced from different families classified as Homopolymer, Random Copolymer and impact Copolymer. In the production process, the operation is in continuous, that means the passage from one degree to another must be done in such a way that the generation of resin with intermediate characteristics, must be the minimum possible. This intermediate resin receives the name of transition, and within a productive process, this transition also has a commercial value, although less than the resins considered prime.

In addition, any failure during transitions process generates a large amount of waste material that represents a significant impact on the environment. That is the reason why from the production process, it is important to reduce the times of transitions by applying different strategies.

Additionally, as an operational approach, any material that is determined as out of specifications is reprocessed in another product with similar characteristics. This paper demonstrated how the optimization of transition times implies a significant reduction of plastic waste avoiding a significant impact on the environment. An environmental analysis is made by applying a Waste reduction algorithm WAR in order to evaluate the impact over the environment of a polypropylene production process applying grade transitions strategies.

It was demonstrated that the transitions reduction can really impact positively reducing possibilities of plastic waste coming directly from the industry

INTRODUCTION

The intensification of the global industrialization, the population explosion, the development of new products and the high production and excessive consumption contributed to the economic development, but resulted in environmental degradation of the ecosystems. In this context, the development of corporate environmentalism, as a strategic part of business, is one of the most significant changes that began to occur in the markets at the beginning of the XXI century. Those actions in the environmental area became proactive and started to be understood as innovations inherent in a competitive strategy of organizations, requiring research and development of sustainable products. [2]

Actually, a broad range of polyolefin applications have forced the polyolefin industry to operate under frequent grade transition policies. This trend has led the polyolefin industry to move away from large continuous production of a single polymer grade to a more flexible production scheme comprising a number of polymer grades of high quality but low volume. In fact, in a polyolefin plant as many as 30–40 polymer grades can be produced. Consequently, under such market-driven operating schedules, the minimization of off -spec polymer production and grade changeover time are prerequisite to any profitability analysis of the process.[3]

In big companies (as for example ESENTTIA, a polypropylene producer in Colombia, South America) when a transition is applied different strategies are made to reduce the amount of transition material. The main tool to improve the transition plans is an Advance process control (APC). When a transition is bad applied off grade material is produced and this material has extra cost and of course an impact over the environment.

A WAR analysis is applied with the objective to evaluate what is the impact when the transition is bad applied and to demonstrate how important s to optimize the transition time. This Tool is an algorithm designed to evaluate the environmental friendliness of only the manufacturing step within this overall framework. The WAR algorithm does not represent a complete life cycle analysis (LCA). The WAR algorithm is simply a tool to be used by design engineers to aid in evaluating the environmental friendliness of a process. This methodology can be used in either the design stage of a future process or in the retrofitting of a current process. For this purpose, the WAR algorithm is to be used in conjunction with chemical process simulators.[4]
This algorithm calculates the potential environmental impact (PEI) of a process, based upon several impact categories[5]:

General Impact category	Impact Category	Measure of impact category
Human Toxicity	Ingestion	LD_{50}
	Inhalation /dermal	OSHA PEL
Ecological Toxicity	Aquatic toxicity	Fathead minnow LC_{50}
	Terrestrial toxicity	LD_{50}
Global atmospheric impact	Global Warming potential	GWP
	Ozone depletion potential	ODP
Regional atmospheric impacts	Acidification potential	AP
	Photochemical oxidation potential	PCOP

This paper aims to demonstrate how the optimization of transition times implies a significant reduction of plastic waste avoiding a significant impact on the environment. An environmental analysis is made by applying a Waste reduction algorithm WAR in order to evaluate the impact over the environment of a polypropylene production process applying grade transitions strategies.

Material and methods.

Industrial plants for polypropylene (PP) production by propylene polymerization are mainly based on Ziegler-Natta catalysts. The active component is titanium chloride (TiCl4) supported on magnesium chloride (MgCl2). An aluminum alkyl (typically triethylaluminium – $Al(C_2H_5)_3$) is used as a cocatalyst, together with the titanium catalyst and different internal donors. These catalytic systems offer polymerization process in conventional slurry (with solvent), as well as in monomer bulk (liquid) or gas phase. [6]
Three kinds of PP are produced in this type of process: Homopolymer, random copolymer and impact copolymer. To produce this materials in a continuous process, transition strategies are applied, where the amount of hydrogen (H_2) is adjusted to obtain different polymer grades, this feature is measured by means of melt flow, which is one of the quality variables controlled in the polymerization process.

In order to evaluate the transition impact over the environment, the polymerization process is simulated in ASPEN PLUS. Actual data of an Homopolymer production is used to apply the simulation, using a propylene supply of 30 ton/h to produce around 24 ton/h of polypropylene. This information is given by ESENTTIA S.A. under confidential restrictions but enough to analyze and understand a real process. A Process flow diagram is showed in the figure 1.

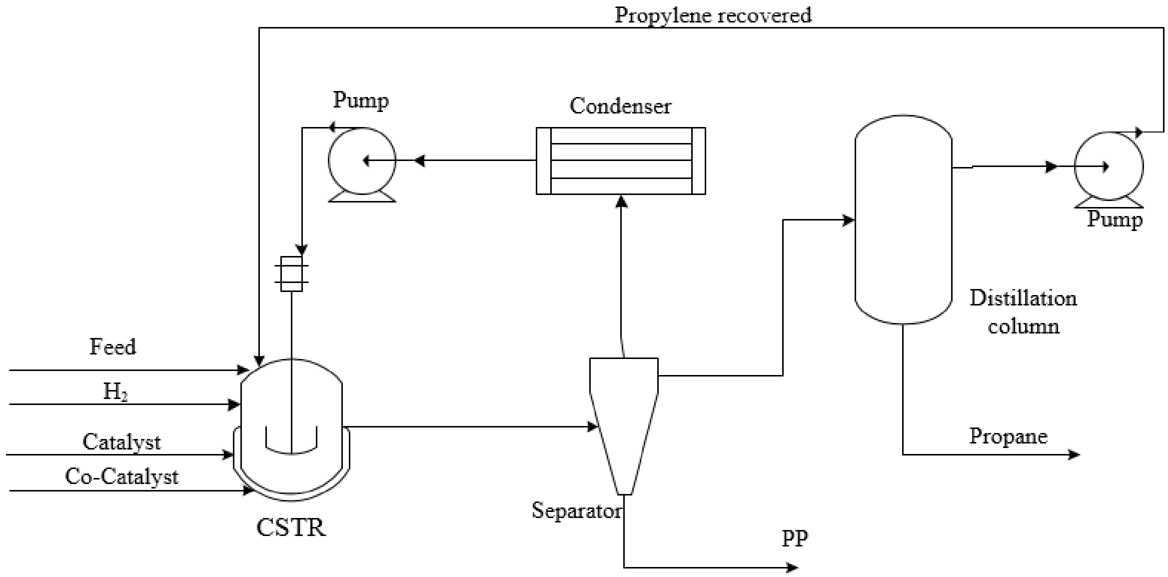

Figure 1. Polypropylene production flowsheet analyzed.

Process begins with the feeding of the main elements to carry on the polymerization reaction. These elements are catalyst (Ziegler Natta), cocatalyst and hydrogen which is used to cut the polymer chains and in this way, control the Melt Flow.
The reactor is assumed to operate at 80°C and 30 barg. As a result of the reaction a powder of PP is obtained and this material is sent to a discharge tank where fines and gases that are carried on with the powder are separated. The gases separated are sent to a splitter to recover the propylene in order to be reused. Products achieved in the process are polypropylene and propane (separated in splitter).

To evaluate the transitions process, the simulation is made considering a change of Melt Flow (MF) passing from 11 to 20. To do this, the flow of H_2 going to the reactor is modified. So, two scenarios are constructed as follow:

Table 1: Case I. 120 TM of transition Polypropylene Production.

Item	**Value**
C_3 Flow (Ton/h)	30
H_2 Flow (gr/h)	2000
Transition time (h)	4
Amount of transition PP (Ton)	120

Table 2: Case II. 240 TM of Transition Polypropylene Production.

Item	**Value**
C_3 Flow (Ton/h)	30
H_2 Flow (gr/h)	2000
Transition time (h)	8

Amount of Transition PP (Ton)	240

According to the information collected, this kind of transitions takes about 8 hours typically, so in the simulation it is considered an improvement of transition by reducing the transition time. That means the transition material will be less than the typical amount of material produced.

Once the simulation in ASPEN is applied, the results obtained are used as an input to evaluate the environmental impact caused by each case presented. The environmental analysis will be made with the Waste Reduction (WAR) algorithm.

In the WAR algorithm it is important to specify the polypropylene according to the characteristics that are shown in Table 3.

Table 3. Polypropylene specifications.

Indicator	**Unit**	**Value**
GWP	kg CO2 eq	2.00
ODP	g CFC-11 eq	n/a3)
AP	g SO2 eq	6.13
POCP	g Ethene eq	0.92
LC50	mg/lt	51.7
LD50	mg/kg	5.000.000
MW	-	350000

Additionally, the energy requirements result from the ASPEN simulation are included in Table 4 for the production basis:

Table 4. Energy requirements for process equipment.

Equipment	**Energy Requirement (MJ/h)**
CSTR Reactor	49908,28
Cyclone	488,47
Condenser	13894,8
Pump	123,24
Distillation column	40993,5
Recycle pumps	41,61
TOTAL	105449,9

In Table 5 the input streams and outputs streams for the WAR analysis are shown.

Table 5. Global streams of process.

INPUT STREAMS	**OUTPUT STREAMS**
Propylene	Polypropylene
Propane	Propane
Hydrogen	Catalyst
Cocatalyst	Cocatalyst
Catalyst	

RESULTS

In both cases the total initial Flow of propylene is 30.338 ton/h. but in table N°6, the value for propylene is 24.78 Ton/h because a calculator block is used in the simulator to calculate the amount of propylene that must be entered into the process to supplement the total raw material flow, taking into account the amount of propylene recovered. Both cases are analyzed as follows:

- **CASE 1. Production of 120 Ton of transition material.** Time transition is 4 hours.
- **CASE 2. Production of 240 Ton of transition material.** Time transition is 8 hours.

Table 6. The input information and the results of WAR analysis are showed for both cases.

Stream / Compound	Inlet [kg/h]				Outlet [kg/h]	
	Propylene	**H_2**	**Catalyst**	**Cocatalyst**	**PP product**	**Propane**
Propylene	24781,30	-	-	-	-	547,39
Propane	124,53	-	-	-	-	125,52
Hydrogen	-	2	-	-	-	-
Catalyst	-	-	1,65	-	1,65	-
Cocatalyst	-	-	-	10	9,96	-
Polypropylene	-	-	-	-	24235,42	-
Total	24905,83	2	1,65	10	24247,04	672,92

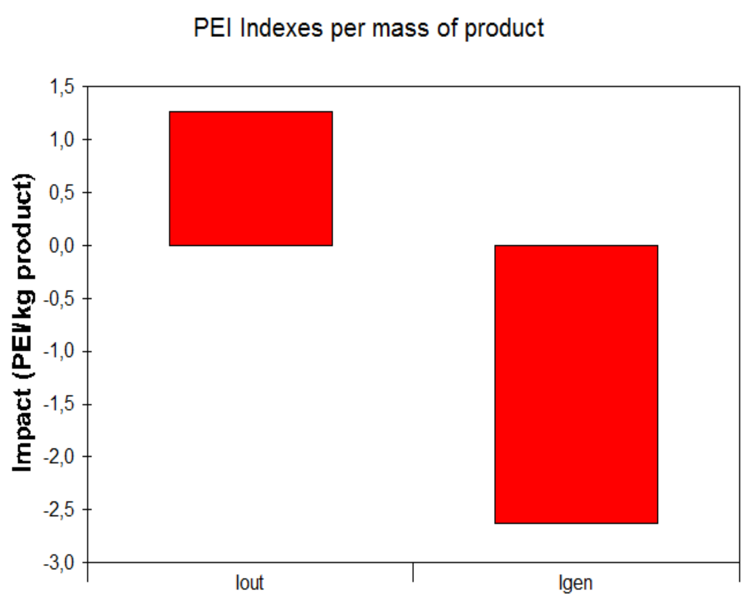

Figure 2. Total rate of potential environmental impact from the process studied.

Figure 2 shows the Potential Environmental Impact (PEI) output and generation per mass for polypropylene production. The results let to highlight that the impact generated by the substances entering the system is reduced by the generation of the polypropylene generated, which is a less dangerous material.

To see the impact of each case presented, the potential environmental impact per kg of product (PEI/kg) result is multiplied by the amount of transition material generated. These results are shown in Table 7.

Table 7. Total rate of potential environmental impact values.

	I_{out}	I_{gen}
Value [PEI/kg]	1.259	-2.631
	I_{out} [PEI]	**I_{gen} [PEI]**
Case 1 (120 TM)	151080	-315720
Case 2 (240 TM)	302160	-631440

By comparing the results for both cases in terms of PEI, and it is clear that by producing more transition material, the double is the impact caused over the environment. As it is shown in the table N°7.

Considering the different aspects that comprising the PEI, figures 3 and 4 show that only two aspects have an important impact, those are PCOP (Photochemical oxidation Potential index) and AP (acidification impact). But like to the result achieved in Global PEI. The negative values of material generated has an effect over the values achieved in PEI leaving.

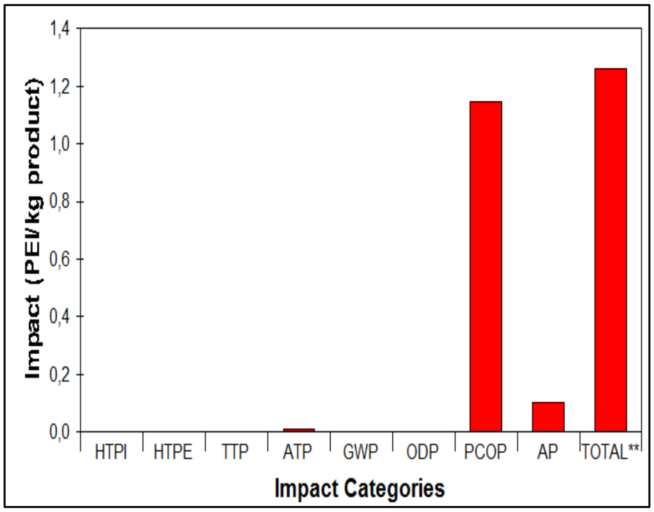

Figure 3. Total output rate of environmental impact for the studied processes. The impact is expressed as the PEI leaving the system per mass of product streams.

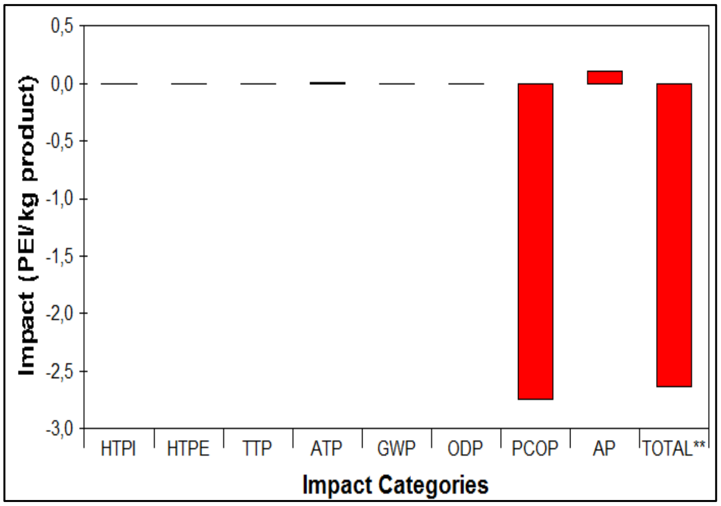

Figure 4. Potential environmental impact generated within the studied processes. The impact is expressed as the PEI generated within the process per mass of product streams.

	120 TM of PP		240 TM of PP.			
Value [PEI/kg]			**Case 1 [PEI]**		**Case 2 [PEI]**	
	I_{out}	I_{gen}	I_{out}	I_{gen}	I_{out}	I_{gen}
HTPI	$2.46*10^{-4}$	$8.76*10^{-5}$	29.52	10.512	59.04	21.024
HTPE	$1.87*10^{-5}$	$-2.76*10^{-4}$	2.244	-33.12	4.488	-66.24
TTP	$8.76*10^{-4}$	$8.76*10^{-5}$	29.52	10.512	59.04	21.024
ATP	$7.74*10^{-3}$	$7.73*10^{-3}$	928.8	927.6	1857.6	1855.2
GWP	$9.12*10^{-4}$	$9.12*10^{-4}$	109.44	109.44	218.88	218.88
ODP	$1.58*10^{-9}$	$1.58*10^{-9}$	$1.896*10^{-4}$	$1.896*10^{-4}$	$3.792*10^{-4}$	$3.792*10^{-4}$
PCOP	1.15	-2.74	138000	-328800	276000	-657600
AP	0.103	0.103	12360	12360	24720	24720

Table 8. Potential indexes report. Case 1 vs case 2.

In Table 8 a comparizon is made between both cases and every potential indexes is evaluated. In case 1 (120 TM of transition material produced) PCOP (photechemical oxidation Potential index) reports the maximun value of 138000. But when the results of PCOP in case 2 (240 TM of transition material produced) is seen, the value is 276000. This means, twice the value report in case 1.

CONCLUSIONS.

Through this analisys it is probed that when the polymerization process transition is improved, the impact over the environment is less. The transition exercise presented in this document is one the most simplest transition made in an industrial polymerization process. There are transitions more complex that can generate a bigger impact over the environment if the process is not well controlled. Nowadays, Esenttia company is applying an advance process control (APC) in order to optimize not only the quality control in the reaction process but also the transitions campaigns when these are applied.
The results observed in the WAR analisys shows first that the negatives values observed in PEI_{gen} (products streams) helps to reduce the impact caused by the materials entering the process.

ACKNOWLEDGMENTS.

The autors express their acknowledgments to ESENTTIA S.A. not only for provide the data but also for provide the support needed to develop the present work. At the same time an special acknowledgment to the support provided by the project agreement ESENTTIA-CNBT

COLCIENCIAS code N° 665173454353 “Desarrollo del Producto y Proceso de producción de Terpolímeros de Propileno-Etileno-Buteno”.

Bibliography.

[1] E. A. Severo, J. C. F. de Guimarães, and E. C. H. Dorion, “Cleaner production and environmental management as sustainable product innovation antecedents: A survey in Brazilian industries,” *J. Clean. Prod.*, vol. 142, pp. 87–97, Jan. 2017.

[2] J. C. F. de Guimarães, E. A. Severo, and P. S. Vieira, “Cleaner production, project management and Strategic Drivers: An empirical study,” *J. Clean. Prod.*, vol. 141, pp. 881–890, Jan. 2017.

[3] Y. Wang, H. Seki, S. Ohyama, K. akamatsu, M. Ogawa, and M. Ohshima, “Optimal grade transition control for polymerization reactors,” *Comput. Chem. Eng.*, vol. 24, no. 2–7, pp. 1555–1561, Jul. 2000.

[4] D. M. Young and H. Cabezas, “Designing sustainable processes with simulation: the waste reduction (WAR) algorithm,” *Comput. Chem. Eng.*, vol. 23, no. 10, pp. 1477–1491, Dec. 1999.

[5] W. M. Barrett, J. van Baten, and T. Martin, “Implementation of the waste reduction (WAR) algorithm utilizing flowsheet monitoring,” *Comput. Chem. Eng.*, vol. 35, no. 12, pp. 2680–2686, Dec. 2011.

[6] E. P. Moore, *Polypropylene handbook : polymerization, characterization, properties, processing, applications*. Hanser Publishers, 1996.