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GESTÃO DE UM PROCESSO DE RECICLAGEM DE POLIURETANOS

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Dissertation presented to the Porto School of Engineering to fulfill the requirements necessary to obtain a Master's Degree in Mechanical Engineering – Industrial Management, under the supervision of Professor Dr. Francisco José Gomes da Silva from Porto School of Engineering and Professor Dr. Artur Jorge Faria Ferreira from University of Aveiro.

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To my parents, brothers and nephews

PALAVRAS CHAVE

Gestão industrial, reciclagem de poliuretano, otimização, ferramentas estatísticas, FMEA

RESUMO

Os poliuretanos (PU) são uma classe de polímeros que devido à sua versatilidade, têm sido utilizados nas mais diversas aplicações. Como tal, a quantidade de desperdícios e resíduos de poliuretano gerados pode resultar em problemas ecológicos e ambientais. Uma vez que a sua deposição em aterros ou a sua incineração não são opções viáveis, estes devem ser reciclados e reutilizados, aumentando assim a sua ecoeficiência.

A presente tese tem como base um processo de reciclagem por via química de PU, desenvolvido a partir de uma parceria entre a SAPEC Química S.A., a Flexipol-Espumas Sintéticas, S.A. e a Universidade de Aveiro. Os pressupostos à escala piloto estão estudados, pelo que é necessário evoluir no sentido de otimizar e controlar o processo com vista à melhoria contínua do processo de reciclagem. Como tal, foram aplicadas ferramentas de gestão industrial (árvore de produto e diagrama de processo), de estatística (análise de variância (ANOVA) e regressão linear) e de qualidade (cartas de controlo e análise de modo e efeitos de falha potencial (FMEA)) ao processo, com vista à sua implementação à escala industrial.

KEYWORDS

Industrial management, polyurethane recycling, optimization, static tools, FMEA

ABSTRACT

Polyurethanes (PU) are a class of polymers, which due to their excellent properties, have been used in a wide variety of applications. In that sense, the quantity of the polyurethane wastes and residues generated may result in ecological and environmental problems. Since landfilling or incineration are not valid options, they must be recycled and be reused, increasing that way its eco-efficiency.

The present thesis is based on the process of chemical recycling of PU, developed from a partnership between SAPEC Química, S.A., Flexipol-Espumas Sintéticas, S.A. and the University of Aveiro. Since the chemical assumptions are studied at the pilot scale, the optimization, control and continuous improvement of the recycling process is now required. As such, industrial (tree of product and process diagram), statistical (analysis of variance (ANOVA) and linear regression) and quality management (control charts and failure mode and effect analysis (FMEA)) tools were applied to the process, aiming their implementation at industrial scale.

LIST OF ABBREVIATIONS, UNITS AND SYMBOLS

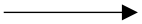
List of abbreviations

Term	Designation
A	Volume of NaOH solution required for titration of the sample
A1	Storage 1
A2	Storage 2
AC	Acid value
ANOVA	Analysis of variance
B	Volume of NaOH solution required for titration of the blank
C1	Control 1
CA	Cleavage agent
CL	Central line
Cp	Process capability
CPL	Process capability based on the lower specification limit
Cpk	Process capability index
CPU	Process capability based on the upper specification limit
D	Detection
df	Degrees of freedom
DOE	Design of experiments
DP	Dependent variable
FMEA	Failure mode and effect analysis
F_{obj}	Objective function
H_0	Null hypothesis
H_1	Alternative hypothesis
IOH	Hydroxyl number
IV	Independent variable
LCL	Lower control limit
LSL	Lower specification limit
MR	Moving range
O	Occurrence
OP1	Operation 1
PU	Polyurethane
PUF	Polyurethane foam
R^2	Linear regression coefficient
RP	Recycled polyol
RPN	Risk priority number
S	Severity
SS	Sum of squares
UCL	Upper control limit
USL	Upper specification limit
VIF	Variance inflation factor
W	Weight of the RP
σ	Standard deviation
$\bar{X}$	Mean

List of units

Property	Unit
A	mL
AC	$mg_{KOH}.g^{-1}$
B	mL
Cost	€.kg^{-1} or €.kW^{-1}
IOH	$mg_{KOH}.g^{-1}$
Temperature	ºC
Time	h
W	g

List of symbols

Term	Designation
	Delay
	Inspection
	Operation
	Storage
	Transport

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PROBLEM DESCRIPTION AND METHODOLOGY

1 PROBLEM DESCRIPTION

The durability and versatility properties of polyurethanes (PU) lead to their use as domestic and industrial applications and even to space travel and medicine. They can be used as: coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants, adhesives, flexible foams and so on. For these reasons, the use of PU has grown impressively over the years (Lee & Ramesh, 2004; Szycher, 2006).

However, the increase in the production of polyurethane foams (PUF) in the past decades, lead to an increase of PUF wastes. Moreover, in its production, circa of 30% of the material does not fulfill the costumers' specifications, so it is considered as waste. In that sense, the disposal of PUF has concerned both scientific and industry community, since landfill and incineration are not acceptable due to ecological and environmental issues (Cregut et al., 2013; Gama et al., 2018; Ohama, 1995). Hence, the concerns about the disposal of PUF wastes can be minimized by its recycling (Aguado et al. 2017; H&S, 2015; Yang et al., 2012; Zia, et al., 2007). In other words, PUF wastes must be recycled and reused to produce new PUF, which is not only a requirement of preventing pollution i.e. environment protection, but is also necessary for the reduction of the cost of production and to enhance the material eco-efficiency.

There are two major categories for the recycling of PUF: mechanical recycling and chemical recycling. In mechanical recycling, the PU wastes are milled and reused without chemical treatment, while the chemical recycling follows the degradation principle (Gama et al., 2018; Zia et al., 2007). Years of research and development lead to many chemical methods for the recycling of PUF, such as: pyrolysis (Terakado et al., 2014), hydrolysis (Brzeska et al., 2015), glycolysis (Aguado et al., 2011; H&S, 2015; Wu et al., 2003; Bolaños et al., 2018), alcoholysis (Bauer, 1991), aminolysis (Bhandari & Gupta, 2018), among others. All these methods have advantages and disadvantages, but the glycolysis is the most commonly used at the industrial scale, because is an economical method and the recycled polyol (RP) can be used in the production of new PUF without affecting its properties. However, normally, the RP obtained by glycolysis is limited to the

production of rigid PUF. In that sense, if it is necessary to obtain RP to be used as raw-material to the production of flexible PUF, the glycolysis can be an invalid option, or at least, this process must be adapted.

Nowadays, a new route or chemical recycling of PUF wastes is emerging which converts the PUF wastes into a liquid, using a cleavage agent (CA). It should be mentioned that the CA used in this method have an acid character. Afterwards, the liquid obtained (recycled polyol, RP) can be used as partial or total substitute of the conventional polyols (main raw-material) in the production of new PUF (Gama et al., 2018), including flexible PUF.

The present thesis is related to the optimization of the industrial process of chemical recycling of PU. This process has been developed as a partnership between SAPEC Química, S.A., Flexipol-Espumas Sintéticas, S.A. and Universidade de Aveiro. Being the chemical aspects of the process already fully developed at the pilot scale, recently subject to a patent request, it is now necessary to look for the industrial management point-of-view, before the process be implemented at industrial scale. In that sense, management (tree of product and process diagram), statistical (ANOVA and linear regression) and quality (control charts and FMEA) tools were used aiming the optimization and continuous improvement of the process. To do so, the following steps were taken:

- First, the process was fully descripted to its better understanding;
- Next, the reaction conditions were optimized to achieve the best characteristics of the RP at the lower cost possible, using a design of experiments (DOE), statistical tools (ANOVA and linear regression) and linear programming;
- After the optimization of the reaction conditions, a set of experiments were conducted and the process was monitored using controls charts and the process capabilities indexes were determined to access information about the reproducibility and the control of the process;
- Finally, actions were recommended to minimize the potential effect of failure of the process and to the continuous improvement of the product quality, using a failure mode and effect analysis (FMEA).

INTRODUCTION

2 INTRODUCTION

Companies, as we know them, dates back almost 100 years, however its concept had changed dramatically. Companies are now facing the globalization of economies and competition which keeps on growing (Pont, 2012). Therefore, industrial managers had to implement quality control, aiming to ensure products with high quality and to improve the manufacturing process efficiency. Yet, is now even more necessary to produce goods at the lowest cost possible, to eliminate nonconformities and their consequences, to eliminate rework and wasted resources, among others (Halevi, 2014). In that sense, some techniques/methods/tools can assist industrial managers to achieve these goals.

2.1 TOOL FOR THE PROCESS DESCRITPION

A process (which can be a production or operating system) consists of a set of inputs which are converted into outputs of higher value. The inputs can be classified as raw-materials, labor, capital, energy or information, while outputs can be goods, services or information. To convert inputs into outputs, it can be necessary transformation operations, controls, transport, flows and storage which are subjected to restrictions/controls (Ávila & Cavaco, 2009; Khedker et al., 2009; Slack et al., 2006).

To understand properly a process, it must be well descripted. A simple method to describe a process is using diagrams. The operating system is represented by the large rectangle, were the inputs enter in the process and leave the system as outputs. Generally, the symbols presented in Table 1 are used to describe a process (among others) (Antony, 2003). The operations are represented by circles, the flow of goods and information by arrows, the storage by triangles and the controls by squares.

Table 1 - List of symbols used to represent the process (Antony, 2003)

Symbol	Description
	Operation
	Transport
	Inspection
	Delay
	Storage

The process diagrams may have some variations of representation, being one of these alternatives, the chaining diagram of the process. From the chaining diagram, it is possible to identify the quantities of raw-materials/components used as well as the sequence of the process. In this type of representation, storage activities are omitted and the flows are represented by links between activities (Ávila & Cavaco, 2009; Sanyal, & Karkare, 2009; Slack et al., 2006). Nonetheless, whatever the term used or differences of representation, the process diagrams, shall give all the necessary information about the process (Ávila & Cavaco, 2009; Sanyal, & Karkare, 2009; Slack et al., 2006).

2.2 OPTIMIZATION OF A PROCESS

To optimize a process, some methods/techniques/tools can be required. Next, tools to optimize a process will be presented, aiming to achieve the best characteristics of a product at the low cost possible, using DOE, statistical tools and linear programming.

2.2.1 DESIGN OF EXPERIMENTS (DOE)

Experiments in manufacturing companies are often conducted in a series of trials or tests which produce quantifiable outcomes. Moreover, for continuous improvement in product/process quality, it is fundamental to understand the process behavior, the amount of variability and its impact on processes (Antony, 2003; Roy, 2001; Ryder, 1990).

Statistical methods play an important role in planning, conducting, analyzing and interpreting data from engineering experiments. The DOE is a powerful technique used

to explore new processes, to gain knowledge of the existing processes, to optimize processes and to achieve world class performance. It was developed in the 1920s by Sir Ronald Fisher at the Rothamsted Agricultural Field Research Station in London. His initial experiments were related to the determination of the effect of various fertilizers on different plots of land (Antony, 2003). Since then, a number of successful applications of DOE have been reported (Antony, 2003; Roy, 2001; Ryder, 1990). The potential applications of DOE in manufacturing processes include (Antony, 2003; Roy, 2001; Ryder, 1990):

- To improve process yield and stability;
- To improve profits and return on investment;
- To improve process capability;
- To reduce process variability and hence better product performance consistency;
- To reduce manufacturing costs;
- To reduce process design and development time;
- To increase the understanding of the relationship between key process inputs and output(s);
- To increase business profitability by reducing waste rate, defect rate, rework, retest;
- Etc.

For the implementation of a DOE, first it is need to stablish an objective. Afterwards, it must be identified the mechanisms and the physical laws affecting this goal. Finally, a list of experiments must be created. More specifically, to carry out a DOE, the following steps must be taken:

- Acquisition of full understanding of the inputs and outputs investigated. A process flow diagram can be helpful;
- Determination of the appropriate measure for the output. A quantitative variable is preferable. Attribute measures (pass/fail) should be avoided. It must ensure that the measurement is stable and repeatable;
- Creation of a design matrix for the factors being investigated. The design matrix must show all possible combinations of high and low levels for each input factor.

The high and low levels can be generically coded as +1 and -1. The levels selected should be realistic and not absurd;

- Perform each experiment and record the results;
- Finally, the data collected can be computed using statistical tools.

2.2.2 ANALYSIS OF VARIANCE (ANOVA) AND LINEAR REGRESSION

ANOVA and linear regression are two of the most used statistical tools, because they can be applied to different types of studies. In 1908, W. S. Gosset applied the t-test to compare the means of two experimental conditions (Rutherford, 2001). In subsequent years, regression and ANOVA were applied by different researchers. Regression was applied to describe and to predict dependent variable (DV) scores from the relations between a predictor and dependent variables (IV) (Rutherford, 2001; Sahai & Ageel, 2000; Scheffé, 1999). In contrast, ANOVA was applied to experimental data from agricultural experiments to determine whether the average scores of groups differed significantly (Rutherford, 2001; Sahai & Ageel, 2000; Scheffé, 1999).

ANOVA is one type of regression analysis and in both cases, the IV scores are obtained from the data collected, while the scores of the DV constitute the model. Subsequently, it uses F-tests to investigate if the mean of DV scores are significantly different. In other words, ANOVA is used to determining how much variation in the DV scores is attributable to differences between the scores obtained from the experimental conditions (the t-test is used to provide statistical significance to the results) (Rutherford, 2001).

The ANOVA can be used to compare means across different groups, between groups and its interaction following the next hypothesis (Randolph & Myers, 2013; Rutherford, 2001):

$$H_0: \mu_1 = \mu_2 = \mu_3 = \mu_k$$
$$H_1: Means\ are\ not\ all\ equal$$

To perform this test, some assumptions were considered, namely: multivariate normality, homoscedasticity and existence of correlation between DV. The hypothesis

tested were: H_0: Means of DV are equal for all the IV; H_1: At least one mean of measures differs significantly from the others (Randolph & Myers, 2013; Rutherford, 2001).

Both regression and ANOVA have no restriction on the number of groups or conditions that may be compared. When only one factor is used, it is called a one-way ANOVA, while if an experiment has two factors, is called a two-way ANOVA. Factorial ANOVA allows to study the influence of two or more IV or factors on a DV. From the ANOVA results, some parameters are obtained, such as (Rutherford, 2001):

- The sum of square (SS) which is defined as the deviation of the observed score from its mean and is determined by:

$$SS = \sum_{i=1}^{n}(X_i - \bar{X})^2 \quad (1)$$

where the X_i is the score of an experiment, $\bar{X}$ is the mean of the scores and n is the number of experiments.

- Degree of freedom (df) represents how many of the scores are able to take different values and is determined by:

$$df = N - 1 \quad (2)$$

where N is the sample size.

- Influence (%) is the influence of the IV on the DV and is determined by the quotient of the IV SS by the sum of the IV SS.

$$Influence\ (\%) = \frac{SS_i}{\sum_i^n SS_i} \quad (3)$$

Linear regression analysis is used to examine relationships between IV and one DV, measured on an interval or ratio scale. In linear regression, the fitting model is represented by a straight line, which connects the means of the IV and DV, in a way that minimizes the sum of the squared distances between the data points and this line. In other words, it involves finding the straight line that best fits the model to the data (Randolph & Myers, 2013; Rutherford, 2001).

The straight line is determined by solving the equation of a straight line (Y = a + b X), in which *Y* is the outcome to predict from *X*, *a* is the intercept of the line for *Y*, *b* is the slope of line for *Y* (its value represents the change in *Y* for each one unit change in *X*) and *X* is the value of the IV. The linear coefficients for two IV are determined by:

$$a = \frac{(\sum IV_2)(\sum IV_1^2) - (\sum IV_1)(\sum IV_1 \times IV_2)}{n(\sum IV_1^2) - (\sum IV_1)^2} \quad (4)$$

$$b = \frac{n(\sum IV_1 \times IV_2) - (\sum IV_1)(\sum IV_2)}{n(\sum IV_1^2) - (\sum IV_1)^2} \quad (5)$$

where IV are the scores of the IV (1 or 2) for various experiments.

Finally, an indicator of goodness of the fit it is R^2 (the regression coefficient) and it is calculated by dividing the model sum of squares (*SS*), by the total sum of squares (Randolph & Myers, 2013). Moreover, the verification of the viability of the results obtained can be access by analyzing the autocorrelation using the Durbin Watson statistic test and/or the multicollinearity of the IVs (Allen, 1997). The Durbin-Watson statistic test scores have values between 0 and 4. A value of 2.0 means that is no detected autocorrelation between IVs, values between 0 and 2 indicate positive autocorrelation between IVs and values between 2 and 4 indicate negative autocorrelation between IVs (Brown, 2002). The Durbin Watson statistic test can be performed using statistical software's, such as the using the IBM SPSS 25. Multicollinearity evaluate intercorrelations or inter-associations among IVs. It is a type of disturbance in the data, and if disturbance is present, the data may not be reliable (Brown, 2002). The determination of multicollinearity (using statistical software's, such as the IBM SPSS 25 Software), is an interactive process. To identify correlation between IVs is determined the variance inflation factor (VIF). VIFs values start at 1 and have no upper limit. A value of 1 indicates that there is no correlation between IVs, VIF values between 1 and 5 suggest that there is a moderate correlation, and VIF values greater than 5 represent critical levels of multicollinearity where the coefficients are poorly estimated (Brown, 2002).

ANOVA and linear regression are two important statistical tools, which allows to identify the influence percentages of each input variable in the output variable and to predict the behavior of the output variable as a function of input variables. Therefore,

they can be used in many engineering and manufacturing applications, to study new or ongoing process. The ANOVA and linear regression can be calculated using the IBM SPSS 25 Software

2.2.3 LINEAR PROGRAMMING

Due to finite resources and time, every process requires optimization. Linear programming is one of the simplest ways to perform an optimization (with given constraints), since it helps to solve very complex optimization problems. It was firstly used in 1826 by Fourier to study linear inequalities (Gass, 2003; Kolman & Robert, 2014; Vanderbei, 2014).

Since real-world problems are most naturally formulated as minimizations or maximizations (i.e. minimize cost or maximize profit), in linear programming, the objective is always to minimize or to maximize a function, called the objective function (F_{obj}) (Gass, 2003; Kolman & Robert, 2014; Vanderbei, 2014).

$$F_{obj} = min\ or\ max\ c_1x_1 + c_2x_2 + \cdots . + c_nx_n \quad (6)$$

where *c* are the values of a given decision variable and *x* are the decision variables. Normally, the optimization problems have constraints, such as the requirement of some decision variable be nonnegative, among others. Moreover, all constraints consist in an inequality (Gass, 2003; Kolman & Robert, 2014; Vanderbei, 2014).

$$a_1x_1 + a_2x_2 + \cdots + a_nx_n \begin{Bmatrix} \leq \\ \geq \end{Bmatrix} b \quad (7)$$

For a problem be solved by linear programming problem, the decision variables, F_{obj}, and constraints must be linear functions. Hence, the linear programming problem, as it will be discussed, can be formulated as follows (Gass, 2003; Kolman & Robert, 2014; Vanderbei, 2014).

Min or Max $c_1x_1 + c_2x_2 + \cdots . + c_nx_n$ (8)

Subject to: $a_{11}x_{11} + a_{12}x_2 + \cdots + a_{1n}x_n \leq b_1$ (9)

$a_{21}x_{21} + a_{22}x_2 + \cdots + a_{2n}x_n \leq b_2$ (10)

. .

$a_{m1}x_{11} + a_{m2}x_2 + \cdots + a_{mn}x_n \leq b_m$ (11)

$x_1, x_2, \ldots\ x_n \geq 0$ (12)

where *m* represents the number of constraints and *n* represents the number of decision variables. Afterwards, the minimization or maximization of the F_{obj} can be achieved using, for example, the OpenSolver.

2.3 MONITORING OF A PROCESS

After optimized and implemented, a process must be monitored. To monitor a process, some methods/techniques/tools can be used. Next, It will then be described how to monitor a process, using controls charts and process capability indexes.

2.3.1 CONTROL CHARTS

A control chart is a graphical tool to monitor an ongoing process. Deviations from the process targets can be detected based on evidence of statistical significance (Xie et al., 2002). Control charts are sometimes referred to as Shewhart control charts, because Walter A. Shewhart (1926) first proposed its theory (Mitra, 2008). Nowadays, control charts are widely used in industry as a tool to monitor the process and several benefits are associated with the use of control charts, such as (Mitra, 2008):

- A control chart indicates when something may be wrong so that corrective action can be taken;
- The pattern of the plot on a control chart diagnoses possible causes and hence indicates possible remedial actions;
- A control chart shows when an exhibited variability is normal and inherent such that no corrective action is necessary;

- If the control chart shows a process to be in statistical control, the capability of the process and its ability to meet customer requirements can be estimated;
- The control chart provides a baseline for instituting and measuring quality improvement. Control charts also provide useful information regarding actions to take for quality improvement.

The values of the characteristic are plotted along the vertical axis while the horizontal axis represents the number of samples. Then, three lines are represented: the central line, which typically represents the average value of the characteristic being plotted, which is an indication of where the process is centered; and the upper and lower control limit lines which are used to make decisions regarding the process. If the characteristic points are within the control limits and do not exhibit any identifiable pattern, the process is said to be under statistical control (Mitra, 2008).

There are many types of control charts and different ways to construct them, such as: *Xbar-Range* chart (which is commonly used when measurements are collected from subgroups of between 2 and 10 observations); *c* chart (used when are used the number of defects per unit, that occurred during the sampling period); *u* chart (similar to a *c* chart, but unlike a *c* chart, an *u* chart is used when the number of samples of each sampling period may vary significantly); *np* chart (used when it is used the total number of defective units with a constant sampling size); *p* chart (used when each unit can be considered pass or fail no matter the number of defects. A *p* chart shows the number of tracked failures (*np*) divided by the number of total units (*n*)); and finally individuals and moving range (*I-MR*) charts (used when the natural subgroup size is unknown, the integrity of the data prevents a clear picture of a logical subgroup, the data is scarce (therefore subgrouping is not yet practical) or when the natural subgroup needing to be assessed is not yet defined) (Berardinelli, 2013).

The *I-MR* charts are the most commonly used control charts for continuous data. It is used when one measurement is collected at each point in time. The *I-MR* control charts are actually two charts, and together they monitor the process average as well as the process variation. The individuals (*I*) chart is used to detect trends and shifts in the process, while the moving range (*MR*) chart shows short-term variability in a process, in

other words it can be used to assessment of the stability of process variation (Berardinelli, 2013).

The setting up of the *I-MR* control charts can be summarized as follows (Berardinelli, 2013; Xi et al., 2002):

- Collect a series of process characteristics through observation;
- Calculate the process characteristics mean ($\bar{X}$) and use it as the central line for the I chart (CL_I);
- Calculate the moving range (*MR*), by:

$$MR_n = |characteristic_n - characteristic_{n-1}| \quad (13)$$

- Calculate the mean of the moving range ($\overline{MR}$) and use it as the central line for the MR chart (CL_{MR});
- Calculate the upper control limit (UCL_I) and the lower control limit (LCL_I) for the *I* chart, by:

$$UCL_I = \bar{X} + \left(\frac{3\overline{MR}}{d_2}\right) \quad (14)$$

$$LCL_I = \bar{X} - \left(\frac{3\overline{MR}}{d_2}\right) \quad (15)$$

where d_2 is a constant which depends on subgroup size (Berardinelli, 2013);

- Calculate the upper control limit (UCL_{MR}) and the lower control limit (LCL_{MR}) for the MR chart, by:

$$UCL_{MR} = \overline{MR} \times d_4 \quad (16)$$

$$LCL_{MR} = \overline{MR} \times d_3 \quad (17)$$

where d_3 and d_4 are a constants which depends on subgroup size (Berardinelli, 2013);

- Plot the central, upper and lower control limit lines, as well as the process characteristics and connect the consecutive points;

- Continue plotting whenever a new measurement is obtained.

Some characteristics of a process that is in control are: most points are near the average; a few points are near the control limits; no points are beyond the control limits. Nonetheless, other aspects must be look at (Pyzdek & Keller, 2003):

- Consecutive points, all on one side of the central average line (i.e. shift);
- Consecutive points, all increasing or decreasing in value (i.e. trend);
- Repeating patterns (i.e. cycles).

2.3.2 PROCESS CAPABILITY

Another tool that statically estimates the performance of a process is the process capability, using the process capability (Cp) and process capability index (Cpk). An ongoing program of quality improvement requires continuous estimation and monitoring of these parameters, which will ensure the best performance that the process is capable to achieve and represents the total variability that exists in the process (Mitra, 2008).

In the process capability analysis, it is assumed that all values of the output quality characteristic are within a distance of 6σ. If a normal distribution for the output quality characteristic is assumed, 99.74 % of the distribution will lie within the bounds of ±3σ on either side of the mean. In that sense, the Cp analyze the mean and standard deviation of the quality characteristic (Halevi, 2014). Moreover, if specification limits are known, the Cp is an easy measurement of the process performance and its ability to meet the specifications. In other words, the Cp analysis can estimate the proportion of nonconforming product and can be calculated by (Mitra, 2008):

$$C_p = \frac{USL - LSL}{6\sigma} \quad (18)$$

$$\sigma = \frac{\overline{MR}}{d_2} \quad (19)$$

where USL is the upper specification limit and the LSL is the lower specification limit.

When Cp = 1, the process spread equals the specification spread, and the process is considered to be barely capable. In that sense, it is desirable to obtain Cp> 1. When Cp> 1, the process can go out of control yet still produce conforming items. In turn, if Cp <1, it implies that the inherent variability in the process, as measured by the process spread 6σ, is greater than the specification spread. For this situation, a process can be in control and still not meet specifications. In Table 2 are listed the recommended minimum values for the Cp.

Table 2 - Recommended minimum values for the process capability indexes (Mitra, 2008)

Process	Two-sided specifications	One-sided specification
Existing process	1.33	1.25
New process	1.50	1.45
Safety, strength, or critical parameter		
Existing process	1.50	1.45
New process	1.67	1.60

Yet, the process variability is not the only parameter that influences a process's ability to produce a conforming product. The location of the process mean is another parameter that affects process capability. Although the Cp does not incorporate the process location, other indexes do, such as the Cpk. Cpk is used when the process means is not at the target value and is determined by (Mitra, 2008):

$$C_{pk} = min\left\{\frac{USL-\bar{X}}{3\sigma}; \frac{\bar{X}-LSL}{3\sigma}\right\} = min\{CPU; CPL\} \quad (20)$$

where CPU is the process capability based on the upper specification limit, the CPL is process capability based on the lower specification limit and $\overline{X}$ is the process characteristics mean.

The Cpk represents the relative distance to three standard deviations (i.e., half the process spread), between the process mean and the closest specification limit. Whereas the Cp represents the process potential, the Cpk represents the capability of

the process with the existing parameter values, i.e., it measures process performance and desirable values are Cpk> 1.

2.4 FAILURE MODE AND EFFECT ANALYSIS (FMEA)

Even if a process is under control and meet the specifications, it is always possible to improve it. The failure mode and effect analysis (FMEA) is an engineering technique used to define, identify, and eliminate known and/or potential failures, problems, errors, and so on, from a system, design, process, and/or service. The FMEA conducted properly will provide useful information that can reduce the risks, before they reach the customer. In fact, FMEA is one of the most important early preventive actions tools, to prevent failures and errors from occurring and reaching the customers (McDermott et al., 2009; Press, 2003; Stamatis, 2003).

In essence, the FMEA is a systematic method to identify all possibilities of failure that can occur and is a living document that is never complete. For each failure, an estimation of its effect, of its occurrence and its detection on the system are made (McDermott et al., 2009; Press, 2003; Stamatis, 2003).

Some benefits of conducting an FMEA are (McDermott et al., 2009; Press, 2003; Stamatis, 2003):

- Helps to define the most significant opportunity for achieving fundamental differentiation;
- Improves the quality, reliability, and safety of the products or service;
- Helps to select alternatives with high reliability and high safety potential during the early phases;
- Improves the company's image and competitiveness;
- Helps to increase customer satisfaction;
- Reduce product development time and costs;
- Helps to identify diagnostic procedures;
- Establishes a priority for design improvement actions;
- Helps to identify critical and/or significant characteristics;
- Helps to define the corrective action;

- Lists the potential failures and identifies the relative magnitude of their effects.

To perform a FMEA, it must be identified, among others (McDermott et al., 2009; Press, 2003; Stamatis, 2003):

- The potential failure mode, which is the problem, the concern, the opportunity to improve, the failure, the reject or the defect;
- The potential effect(s) of failure, which is the consequence of the failure on the next process, operation, product, customer, and/or government regulations;
- The potential cause(s) of failure, which is the process deficiency that results in the failure mode.

Moreover, since the essence of the FMEA is to identify and prevent known and potential problems, some assumptions have to be made, such as that problems have different priorities. There are three components that help define the priority of failures (McDermott et al., 2009; Press, 2003; Stamatis, 2003):

- Occurrence (O);
- Severity (S);
- Detection (D).

Occurrence is the frequency of the failure. Severity is the seriousness (effects) of the failure. Detection is the ability to detect the failure before it reaches the customer. There are many ways to define the value of these components. The usual way is the use of numerical scales (called risk criteria guidelines). The ranking for these criteria's can have any value, nonetheless, the ranking of 1 to 10 is widely used and it is highly recommended because is easier to interpret and provides high accuracy and precision in the quantification of the rankings. The rank guidelines for process FMEA are listed in the following tables (Stamatis, 2003).

Table 3 - Occurrence guideline for FMEA process (Stamatis, 2003)

Detection	Criteria	Rank
Almost certain	Failure almost certain. History of failures exists from previous or similar designs	10
Very high	Very high number of failures likely	9
High	High number of failures likely	8
Moderately high	Frequent high number of failures likely	7
Medium	Moderate number of failures likely	6
Low	Occasional number of failures likely	5
Slight	Few failures likely	4
Very slight	Very few failures likely	3
Remote	Rare number of failures likely	2
Almost never	Failure unlikely. History shows no failures	1

Table 4 - Severity guideline for FMEA process (Stamatis, 2003)

Effect	Criteria	Rank
Hazardous	Hazardous effect. Safety-related—sudden failure. Noncompliance with government regulation	10
Serious	Potential hazardous effect. Able to stop product without mishap; safety-related; time-dependent failure. Disruption to subsequent process operations. Compliance with government regulation is in jeopardy	9
Extreme	Customer very dissatisfied. Extreme effect on process; equipment damaged. Product inoperable but safe. System inoperable.	8
Major	Customer dissatisfied. Major effect on process; rework/repairs on part necessary. Product/process performance severely affected but functional and safe. Subsystem inoperable	7
Significant	Customer experiences discomfort. Product/process performance degraded, but operable and safe. Nonvital part inoperable	6
Moderate	Customer experiences some dissatisfaction. Moderate effect on product/process performance. Fault on nonvital part requires repair	5
Minor	Customer experiences minor nuisance. Minor effect on product/process performance. Fault does not require repair. Nonvital fault always noticed	4
Slight	Customer slightly annoyed. Slight effect on product or process performance. Nonvital fault noticed most of the time	3
Very slight	Customer more likely will not notice the failure. Very slight effect on product/process performance. Nonvital fault noticed sometimes	2
None	No effect on product or subsequent processes	1

Table 5 - Detection guideline for FMEA process (Stamatis, 2003)

Detection	Criteria	Rank
Almost impossible	No known controls available to detect the failure	10
Remote	Remote likelihood current controls will detect the failure	9
Very slight	Very slight likelihood current controls will detect the failure	8
Slight	Slight likelihood current controls will detect the failure	7
Low	Low likelihood current controls will detect the failure	6
Medium	Medium likelihood current controls will detect the failure	5
Moderately high	Moderately high likelihood current controls will detect the failure	4
High	Good likelihood current controls will detect the failure	3
Very high	Very high likelihood current controls will detect the failure	2
Almost certain	Current controls almost always will detect the failure. Reliable detection controls are known and used in similar processes	1

The priority to solve the problems is articulated via the risk priority number (RPN). This number is a product of the occurrence, severity, and detection and the maximum number possible for the RPN is 1000 (10, 10, 10, from occurrence, severity, and detection). The RPN is determined by:

$$RPN = O \times S \times D \tag{21}$$

RPN shall be used to rank the order of the concerns and it is defined as a minor, moderate, high, and critical risk. Under minor risk, no action is taken; under moderate risk, some action may take place; under high risk, definite action must take place; under critical risk, definite actions will take place and extensive changes are required.

If there are more than two failures with the same RPN, failure with high severity must first be addressed. Examples of cases which corrective action are to be taken are shown in Table 6 (Stamatis, 2003).

Table 6 - Cases where corrective action are to be taken (Stamatis, 2003)

Assessment rating			Causes of failure	Action taken?
Occurrence (O)	Severity (S)	Detection (D)		
1	1	1	Ideal situation	No
1	1	10	Assured mastery	No
1	10	1	Failure does not reach the user	Yes
1	10	10	Failure reaches user	Yes
10	1	1	Frequent fails detectable, costly	Yes
10	1	10	Frequent fails reaches the user	Yes
10	10	1	Frequent fails with major impact	Yes
10	10	10	Trouble	Yes

Besides the examples listed above, actions should be applied to failure modes with a severity of 9 or 10, or depending on the RPN of each potential failure mode. In the last case, the manager can define a limit value, for which the RPN is acceptable. If actions are taken, the FMEA must be reevaluated. The consequences of severity, occurrence, and detection shall be determined, as well as calculate the RPN and the failures ranked again.

RESULTS

3 RESULTS

The present thesis aims the optimization of a process of PU chemical recycling, before of the *scale-up*. In that sense, the process will be described to a better understanding of it and the reaction conditions will be optimized to achieve the best characteristics of the recycled polyol (RP) at the low cost possible, using a design of experiments (DOE), statistical tools (ANOVA and linear regression) and linear programming. Finally, the process will be monitored using control charts and the process capabilities indexes and actions will be recommended aiming the continuous improvement of the product quality.

3.1 OPTIMIZATION OF THE REACTION CONDITIONS

3.1.1 PROCESS DESCRIPTION

As mentioned, this thesis discusses the industrial management of a chemical recycling method of PU. More specifically, the recycling of PU is achieved by a chemical reaction between PU wastes and a cleavage agent (CA). After the reaction, a viscous liquid is obtained, named as RP, which can be used to produce new PU. To recycle PU accordingly to the method discussed, a CA is needed. So, the weight ratio of PU/CA, named as Ratio, is of fundamental importance in the RP quality. Also, the reactions conditions such as Temperature and Time are extremely important, to obtain a RP with suitable properties to be used to produce new PU. These assumptions are based on previous knowledge acquired in a PT2020 project. In Figure 1 is presented the tree diagram of RP.

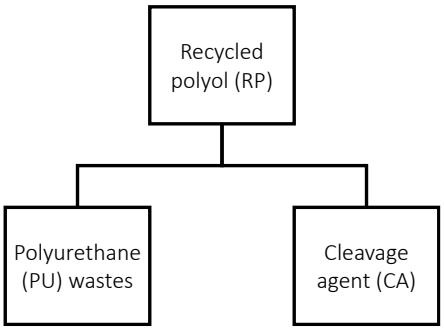


Figure 1 - Tree of product

Rigorous knowledge of the process allows a better understanding of the addressed study, helping to its optimization and affords a more realistic notion of it. In that sense, the process diagram is presented in Figure 2, following the symbology showed in Table 1. As can be seen from Figure 1 and Figure 2, the recycling method presented can be performed by a simple process. It starts by storing the raw-materials (PU and CA) in a warehouse (A1). Next, as needed, the PU and the CA goes throw an operation (OP1), which is the chemical reaction. Afterwards, the properties (hydroxyl number, IOH, and acid value, AC) of the RP are measured in an inspection unit (C1). Finally, the RP is stored (A2) till expedition.

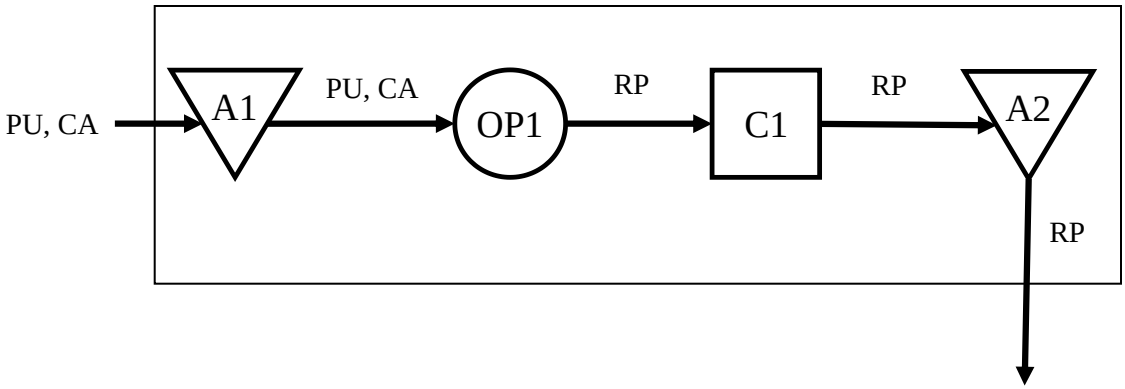


Figure 2 - Process diagram of the studied recycling method

For the optimization of the reaction conditions, first was establish a DOE. Next, the set of experiments were conducted and the data collected was statistically evaluated using ANOVA and linear regression. Finally, since the objective is to achieve the best characteristics of a product at the low cost possible, linear programming was used.

3.1.2 DOE

To perform a DOE, first is needed to clearly define the objective of the study. In the present case, the objective is to identify how the properties of the RP are influenced by the reaction conditions. Afterwards, the process variables (inputs and outputs) were selected. Based on the knowledge previous acquired in a PT2020 project, the Ratio (weight ratio of PU/CA), reaction Temperature and the reaction Time are the reaction parameter which influences the properties of RP, obtained by this PU recycling method. Despite of the absence of reports regarding this recycling method, the weight ratio of PU/CA, reaction Temperature and the reaction Time were also used as factors, to study the influence of the reaction parameters of the glycolysis of PU, by Aguado et al., (2011) or by Hekmatjoo et al., (2015).

The output variables selected were the IOH and the AC of the RP, because accordingly with industrial partners, these are two of the most important properties of polyols for the PU manufactures. Next, lower and higher levels must be imposed on the input variables. Levels selection requires in-depth knowledge of the process and their combination must be suitable to produce a RP with suitable properties to produce PU. The lower and higher levels of input variables were selected based on previous knowledge acquired in a PT2020 project, as mentioned, and are presented in Table 7.

Table 7 - Design matrix for the factors being investigated

Input variable	Lower level	Higher level
Ratio	4.0	5.0
Temperature (°C)	190	200
Time (h)	4.5	5.5

As can be seen in Table 7, only two levels of each factor were selected. Despite more levels may result in more accurate data, it can required high quantities of reactants. Therefore, taking into account the costs and time needed, only two levels were selected. Moreover, since the selection of the level values was based on previous knowledge acquired in a PT2020 project, they are refined. Therefore, the differences between the lower and higher levels are small.

All combinations of the reaction conditions presented in Table 7 were used and the properties of the obtained RP are presented in Table 8 (the methodology of production of RP and its characterization are presented in Appendix I). From the results presented in Table 8, it can be seen that the IOH varies from 47.7 $mg_{KOH}.g^{-1}$ up to 53.6 $mg_{KOH}.g^{-1}$, while the AC varies from 2.4 $mg_{KOH}.g^{-1}$ up to 3.5 $mg_{KOH}.g^{-1}$. Also, some trends can be observed, since higher Ratio, higher reaction Temperatures or higher reaction Times, thus RP with higher IOH and lower AC.

Table 8 - Full factorial design (2^3) for experiments and respective RP properties

Reaction	Weight Ratio of PU/CA	Temperature (°C)	Time (h)	IOH ($mg_{KOH}.g^{-1}$)	AC ($mg_{KOH}.g^{-1}$)
1	4.0	190	4.5	47.7 ± 0.1	3.5 ± 0.3
2	4.0	190	5.5	48.1 ± 0.3	3.4 ± 0.2
3	4.0	200	4.5	51.0 ± 0.4	2.7 ± 0.2
4	4.0	200	5.5	51.1 ± 0.2	2.6 ± 0.3
5	5.0	190	4.5	49.1 ± 0.4	3.3 ± 0.1
6	5.0	190	5.5	51.0 ± 0.4	3.1 ± 0.2
7	5.0	200	4.5	53.4 ± 0.2	2.5 ± 0.1
8	5.0	200	5.5	53.6 ± 0.1	2.4 ± 0.2

Due to the absence of data in the literature, regarding the effect of the reaction conditions on the properties of RP using this recycling method, the results presented in Table 8 were compared with those obtained using glycolysis (most commonly used method for the recycling of PU). Nonetheless, mention must be paid to the fact that glycolysis is a significantly different process and using glycolysis, the RP has different range of IOH and AC.

According to Hekmatjoo et al. (2015), who modeled the glycolysis of flexible PUF wastes using an artificial neural network methodology, reported that the IOH of the RP increased by decreasing the weight ratio of PU/CA, which is not in agreement with the trend observed in Table 8. Murai et al., (2003), who studied the glycolysis of rigid PUFs under various reaction conditions, reported that the depolymerization of PU is faster using higher temperatures. Likewise, Molero et al., (2006), who recovered polyols from flexible PUF using glycolysis, reported that as the time reaction progresses, the PU structure is degraded and converted into smaller fragments (urethane oligomers),

releasing polyol to the reaction media. In both cases, it can be concluded that using higher reaction temperatures or higher reaction times, results in more OH groups present in the RP, which is in agreement with the trends observed in Table 8.

Nonetheless, according to the data reported by H&S (2015), the obtained RP presents an IOH between 45-49 $mg_{KOH}.g^{-1}$ and an AC lower than 1.1 $mg_{KOH}.g^{-1}$. Comparing the results presented in Table 8 to those reported by H&S, it can be observed that the IOH values are similar. Regarding the AC values, it can be observed that the results presented in Table 8 are 2 or 3 times higher, but these values are still suitable for the production of PU. Still, the reactions conditions are not specified by H&S and the type of PU has a great influence on the properties of the RP, which can justify the small differences observed.

From the results presented in Table 8, it can also be seen that the reaction conditions leading a RP with higher and lower IOH are, respectively, 8 and 1, while the same conditions leads a RP with lower and higher CA. Thus, it can be observed that the IOH and AC are inversely proportionally. As mentioned in the problem description section, the CA used in this method has an acid character. In that sense, it is confirmed that higher content of polyol (higher IOH), is associated with the consumption of the CA (lower AC).

Despite the effect of the reaction conditions on the properties of the RP was evaluated, their influence on the properties of the RP was not statistically evaluated.

3.1.3 ANOVA

The ANOVA was used to statistical evaluate the effect of each reaction condition on the properties of the RP. The data obtained previously was computed using the IBM SPSS 25 Software and in Table 9 and Figure 3 are presented the sum of squares (SS), the degrees of freedom (df) and the percentage of influence of each reaction conditions on the IOH of the RP. In Table 10 and Figure 4 are presented the sum of squares (SS), the degrees of freedom (df) and the percentage of influence of each reaction conditions on the AC of the RP.

Table 9 - Effect of reaction parameters on the IOH of the RP

Independent Variables (IV)	Sum of squares (SS)	Degrees of freedom (df)	Influence (%)
Ratio	10.77	1	31.5
Temperature (°C)	21.32	1	62.4
Time (h)	0.93	1	2.7
Ratio*Temperature (°C)	0.06	1	0.2
Ratio*Time (h)	0.33	1	1.0
Temperature*Time (°C.h)	0.52	1	1.5
Ratio*Temperature*Time (°C.h)	0.22	1	0.7
TOTAL	34.14	7	100.0

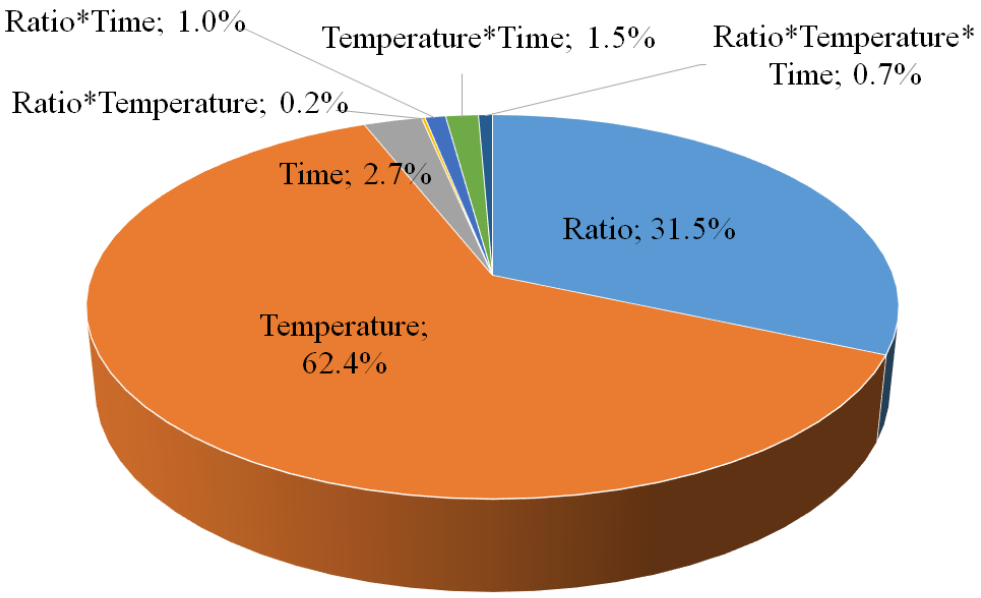


Figure 3 - Relative effect of the reaction conditions on the IOH of the RP

Table 10 - Effect of reaction parameters on the AC of the RP

Independent Variables (IV)	Sum of squares (SS)	Degrees of freedom (df)	Influence (%)
Ratio	0.26	1	10.3
Temperature (°C)	0.42	1	16.4
Time (h)	0.38	1	15.0
Ratio*Temperature (°C)	1.02	1	39.7
Ratio*Time (h)	0.14	1	5.4
Temperature*Time (°C.h)	0.27	1	10.6
Ratio*Temperature*Time (°C.h)	0.07	1	2.6
TOTAL	2.56	7	100.0

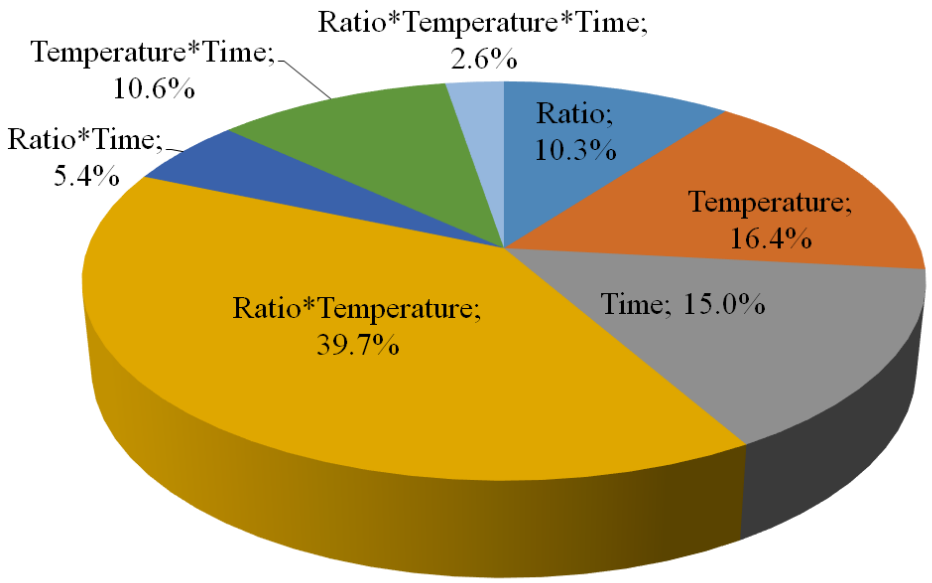


Figure 4 - Relative effect of the reaction conditions on the AC of the RP

From the ANOVA results, it can be seen that Temperature and Ratio are the input variables with higher influence on the IOH of the RP. The Temperature has an influence of 62.4%, while Ratio has an influence of 31.5%. Together, Temperature and Ratio have a 93.9% influence on the IOH of the RP, meaning that if, it is necessary to obtain a RP with higher or lower IOH, these are reactions parameters which should be adjusted.

Regarding the influence of the reaction conditions on the AC of the RP, distinct results were obtained. From the ANOVA results, it can be seen that the AC is not influenced by a particular factor. Instead, it is dependent on several factors and their interactions, with similar influence, meaning that adjustments on the AC can be difficult to control. Nonetheless, the major influence on the AC is the combination of Ratio and Temperature, with an influence of 39.7%.

Again, the ANOVA results were compared with those obtained using glycolysis, and different results are reported in literature. In the examples presented next, it was studied the influence of the glycolysis reaction conditions on the yield of polyol. As explained previously, higher yields of polyol are associated with higher IOH and lower AC. Aguado et al., (2011), reported that the PU/CA Ratio is the most significant factor, with an influence of 40%. Regarding the reaction Temperature, it was reported a 14% of influence. Similarly, Aguado et al., (2017), who recycled PUF from shoe soles via glycolysis, reported that the PU/CA Ratio is the most significant factor with an influence of 29%. The reaction Temperature presented an influence of 23%, while the reaction Time had an influence of 18%. As can be seen from the results presented in the literature, the glycolysis of PU is significantly different, when compared with this method.

3.1.4 Linear regression

After statistical evaluated the effect of the reaction conditions on the properties of the RP, linear regression was applied to the DOE results, in order to determine linear functions, which relates the effect of the reaction conditions on the properties of the RP, using the IBM SPSS 25 software. In Table 11 are listed the linear regression coefficients for the effect of the reaction conditions on the IOH and AC.

Table 11 – Linear regression coefficients of the reaction conditions effect on the IOH and on the AC of the RP

	IOH	AC
Constant	-26.885	19.236
Ratio	2.32	-0.193
Temperature (°C)	0.327	-0.076
Time (h)	0.68	-0.132

With the results presented in Table 11, it was possible to determine the dependence of IOH and AC on the reaction conditions:

$$\begin{cases} IOH = -26.885 + 2.32 \times Ratio + 0.327 \times Temperature + 0.68 \times Time \\ AC = 19.236 - 0.193 \times Ratio - 0.076 \times Temperature - 0.132 \times Time \end{cases} \quad (22)$$

Analyzing the results presented in Table 11, it can be seen that higher Ratio, higher reaction Temperature or higher reaction Time, contributes to the increase of the IOH of RP (coefficients with positive signs). In other words, the increase of these reactions conditions, increase the yield of RP. In turn, higher Ratio, higher reaction Temperature or higher reaction Time, contributes to the decrease of the AC of RP (coefficients with negative signs), which is associated with the consumption of CA (acid character).

Before these functions be used in linear programming, it was evaluated if they are representative of the process. Therefore, the linear regression results were evaluated using the Durbin Watson statistic test and analyzed the multicollinearity between IVs, being the results presented in Table 12 and in Table 13, respectively.

Analyzing the Durbin-Watson statistic test results presented in Table 12, it can be observed scores of 2.095 and 0.931 for IOH and AC, respectively. Regarding the IOH, it can be considered that no detected autocorrelation between IVs were detected. In turn, the AC scores suggest that exist positive autocorrelation between IVs (Allen, 1997). Moreover, analyzing the multicollinearity between IVs results presented in Table 13, it can be observed that most of the VIF values are near 1, indicating that there is no correlation between the IVs. However, the VIF scores of the Ratio/Temperature, Time/Ratio and Time/Temperature, indicates that exist moderate or high correlation between this IVs (Brown, 2002).

Table 12 - Durbin Watson statistic test

DV	Value
IOH	2.095
AC	0.931

Table 13 - Multicollinearity between IVs

IOH			AC		
DV	IV	VIF	DV	IV	VIF
Ratio	Temperature	2.792	Ratio	Temperature	1.239
	Time	1.078		Time	1.218
Temperature	Ratio	1.479	Temperature	Ratio	1.138
	Time	1.041		Time	1.201
Time	Ratio	6.238	Time	Ratio	1.140
	Temperature	11.373		Temperature	1.224

Despite of the Durbin Watson statistic test and the multicollinearity between IVs results suggest that the linear regression coefficients could be poorly estimated, to access the viability of the linear regression functions, they were used to estimate predicted values. In that sense, different levels of the input variables were used to calculate the predicted values of IOH and AC. Afterwards, predicted and experimental values were plotted and compared. The relationship between the experimental and predicted of IOH and AC of the RP are presented in Figure 5 and Figure 6, respectively.

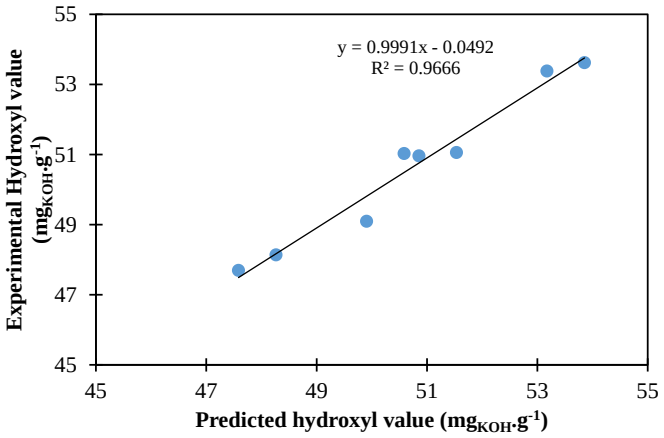


Figure 5 - Relationship between experimental and predicted IOH of the RP

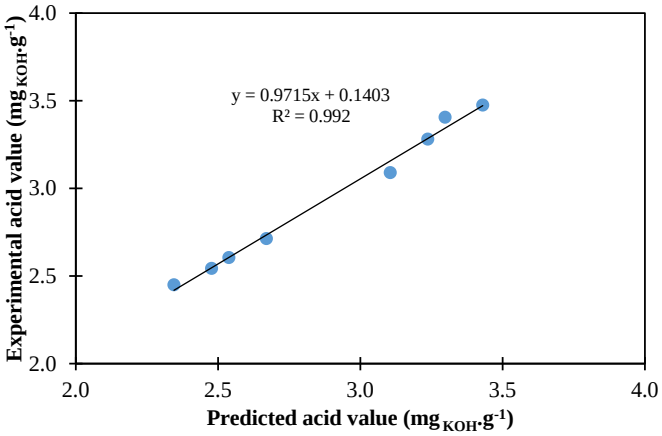


Figure 6 - Relationship between experimental and predicted AC of the RP

From the results presented in Figure 5 and Figure 6, it can be seen that the relationship between the experimental and the predicted values of the IOH have a correlation (R^2) of 0.9666, while the experimental and the predicted values of the AC have a correlation (R^2) of 0.9920. In other words, it was observed that the process conditions, highly correlate the experimental and the predicted values of the IOH and AC, meaning that they can be used to optimize the reaction conditions.

3.1.5 LINEAR PROGRAMMING

A linear program can contain multiple variables and solving them graphically or algebraically can be difficult (Berardinelli, 2013). To overcome this issue, is commonly to use OpenSolver (an open source linear and optimizer for Microsoft Excel).

To optimize the recycling conditions using linear programming, since the objective is to minimize the recycling process costs, first was identified the decision variables, namely Ratio, Temperature and Time, according to the previous sections. Next, it was written the F_{obj}, in which the cost of each variable was determined (see Appendix II).

$$F_{obj} = -1.352 - 0.060 \times Ratio + 0.007 \times Temperature + 0.087 \times Time \quad (23)$$

Afterwards, it was written the constraints. Constraints (*a*) to (*f*) are related to the reaction conditions, namely (*a*) and (*d*) limit the Ratio between 4.0 and 5.0; (*b*) and (*e*) limit the Temperature between 190 and 200 ^{o}C; (*c*) and (*g*) limit the Time between 4.5 h

and 5.5 h. In turn, constraints (*g*) to (*i*) are related to the properties of the RP, namely constraints (*g*) and (*h*) limit the IOH between 44.1 and 53.4 $mg_{KOH}.g^{-1}$, while constraining (*i*) limit the AC below 3.0 $mg_{KOH}.g^{-1}$ (imposed by customers). Note that, the constraint functions used to limit IOH and AC of the RP are derived from the linear regression results.

Finally, as mentioned, OpenSolver was used to minimize the F_{obj}, by varying the scores of Ratio, Time and Temperature. The scores achieved (optimal solution) are the reaction conditions which minimize the recycling cost, accomplishing the customer requirements for the RP. The linear programming results are presented in Table 14, where it can be observed that the response of the linear programming (F_{obj}) is 1.1 $€.kg^{-1}$, i. e., the minimal cost to obtain the RP, attending the properties requirements. Accordingly to Flexipol-Espumas Sintéticas, S.A., the price of the conventional polyol is around 1.6 $€.kg^{-1}$. Moreover, from the H&S (2015), the price of the RP is 1.12 $€.kg^{-1}$. Therefore, it can be observed that the price of RP is lower or similar to those obtained from petroleum feedstocks or obtained from alternative recycling processes, respectively.

Table 14 - Linear programming results

		Others	Ratio	Temperature (°C)	Time (h)	F_{obj}		
Minimize		-1.352	-0.060	0.007	0.087			
Optimal solution			5.0	193.1	4.5	1.1		
Subject to	(a)		1			5.0	<=	5.0
	(b)			1		193.1	<=	200
	(c)				1	4.5	<=	5.5
	(d)		1			5.0	>=	4.0
	(e)			1		193.1	>=	190
	(f)				1	4.5	>=	4.5
	(g)	-26.885	2.32	0.327	0.68	50.9	>=	44.1
	(h)	-26.885	2.32	0.327	0.68	50.9	<=	53.4
	(i)	19.236	-0.193	-0.076	-0.132	3.0	<=	3.0

From the linear programming results, to achieve the optimal solution, the following reaction conditions must be used:

- Ratio – 5.0;
- Temperature – 193.1°C;

- Time – 4.5h.

Finally, from the results presented in Table 14, it can be seen that the IOH and the AC of the RP, fulfill the costumer's requirements, presenting values of 50.9 $mg_{KOH}.g^{-1}$ and 3.0 $mg_{KOH}.g^{-1}$, respectively. Comparing again the properties of the RP obtained by linear programming, to those reported by H&S, it can be observed that the IOH values are similar (the H&S RP presents an IOH between 45-49 $mg_{KOH}.g^{-1}$). The AC values are 3 times higher (the H&S RP presents an AC lower than 1.1 $mg_{KOH}.g^{-1}$), but accordingly with the PU manufactures partners, these values are still suitable for the production of PU.

3.2 MONITORIZATION OF THE RECYCING OF PUF

Variability is present in any process, no matter how sophisticated it is. Industrial managers must be aware of it and this can be accomplished using process control, through control charts. In that sense, a set of experiments using the same conditions were conducted and the capability of the process to achieve the costumers' requirements was statistically evaluated, using control charts and analyzing the process capability indexes.

3.2.1 CONTROL CHARTS

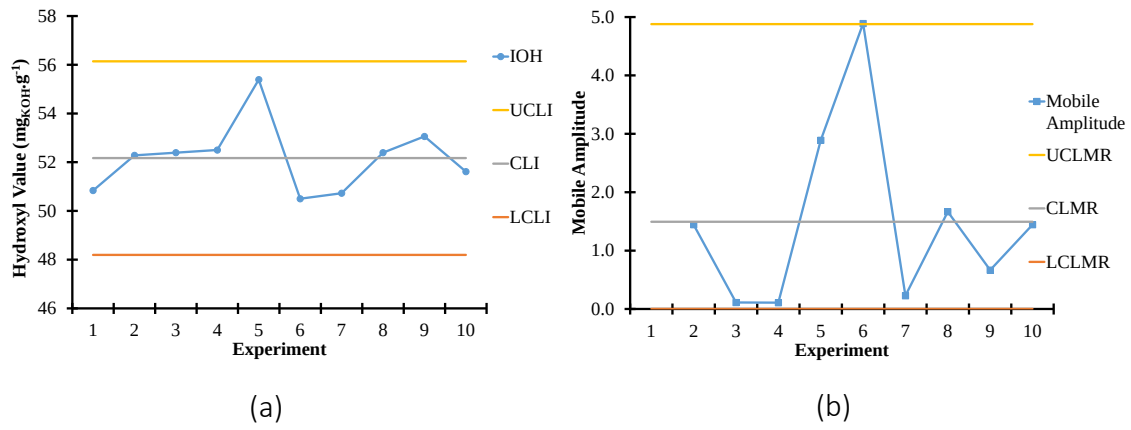
After determined the optimal reaction conditions, a set of 10 experiments were conducted to evaluate if the process is statistically under control. In Table 15 and Table 16 are listed the *I-MR* control charts results of IOH and AC, and the respective plots are present in Figure 7 and Figure 8.

Table 15 - Control chart results of the IOH, with the upper control limit (UCL), central line (CL) and lower control limit (LCL) of individuals (I) and moving range (MR)

Experiment	IOH	Mobile Amplitude	UCL_I	CL_I	LCL_I	UCL_{MR}	CL_{MR}	LCL_{MR}
1	50.8		56.1	52.2	48.2	4.9	1.5	0.0
2	52.3	1.4	56.1	52.2	48.2	4.9	1.5	0.0
3	52.4	0.1	56.1	52.2	48.2	4.9	1.5	0.0
4	52.5	0.1	56.1	52.2	48.2	4.9	1.5	0.0
5	55.4	2.9	56.1	52.2	48.2	4.9	1.5	0.0
6	50.5	4.9	56.1	52.2	48.2	4.9	1.5	0.0
7	50.7	0.2	56.1	52.2	48.2	4.9	1.5	0.0
8	52.4	1.7	56.1	52.2	48.2	4.9	1.5	0.0
9	53.1	0.7	56.1	52.2	48.2	4.9	1.5	0.0
10	51.6	1.4	56.1	52.2	48.2	4.9	1.5	0.0
Mean	52.2	1.5						

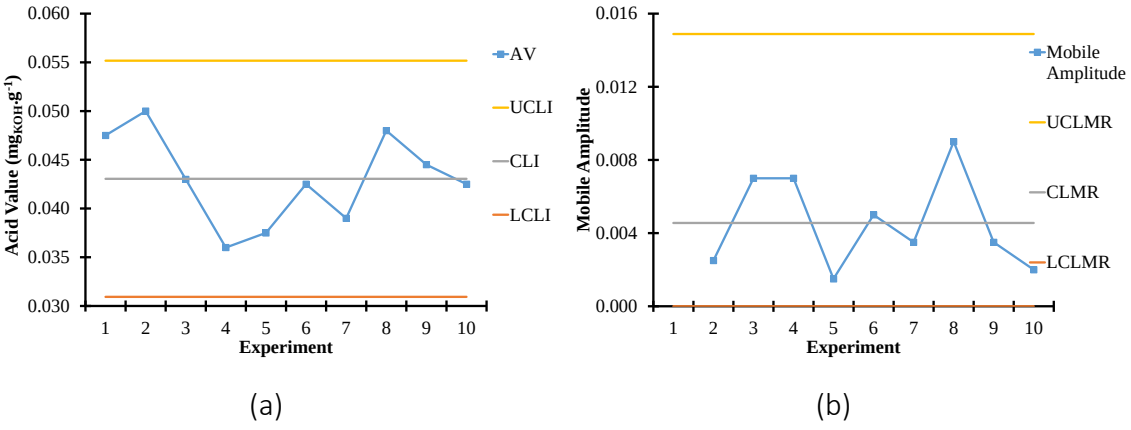
Table 16 - Control chart results of the AC, with the upper control limit (UCL), central line (CL) and lower control limit (LCL) of individuals (I) and moving range (MR)

Experiment	IOH	Mobile Amplitude	UCL_I	CL_I	LCL_I	UCL_{MR}	CL_{MR}	LCL_{MR}
1	0.05		0.055	0.043	0.031	0.015	0.005	0.000
2	0.05	0.003	0.055	0.043	0.031	0.015	0.005	0.000
3	0.04	0.007	0.055	0.043	0.031	0.015	0.005	0.000
4	0.04	0.007	0.055	0.043	0.031	0.015	0.005	0.000
5	0.04	0.002	0.055	0.043	0.031	0.015	0.005	0.000
6	0.04	0.005	0.055	0.043	0.031	0.015	0.005	0.000
7	0.04	0.004	0.055	0.043	0.031	0.015	0.005	0.000
8	0.05	0.009	0.055	0.043	0.031	0.015	0.005	0.000
9	0,04	0.004	0.055	0.043	0.031	0.015	0.005	0.000
10	0,04	0.002	0.055	0.043	0.031	0.015	0.005	0.000
Mean	0.04	0.005						



(a) (b)

Figure 7 – I (a) and MR (b) control charts of the IOH



(a) (b)

Figure 8 - I (a) and MR (b) control charts of the AC

A control chart represents the evolution of a characteristic process over time and for a process to be considered statistically under control: *i*) most points must be near the average (CL); *ii*) a few points must be near the control limits; and *iii*) no points must be located beyond the control limits (Berardinelli, 2013). Analyzing Figure 7 and Figure 8, it can be observed that the values of IOH and AC predominantly oscillates in randomly around the central line and within the control limits.

The individual chart (*I* chart) is used to detect trends and the results presented in Figure 7 a) suggests a possible trend that may occur, since the IOH increase continuously in the first five experiments and again from the 6th to the 9th. Moreover, it can also be observed in the *MR* control chart of the IOH (Figure 7 b)). In this, there are some points near to the control limits. The *MR* chart provide information about short-term variability in a process. In other words, it can be used to assess the stability of process variation. In

that sense, it can be considered that the IOH of the different experiments present some variability, which can affect the stability of the process.

Despite some anomalies detected, the process can be considered under control. Nonetheless, further information was collected to analyze if the process is reliable and accurate.

3.2.2 PROCESS CAPABILITY

Besides the analysis of process control through control charts, the process capability indexes were determined. The process capability (Cp) represents whether the distribution can fit within the specifications, while the process capability index (Cpk) represents whether the overall average is centrally located. The calculated values of the Cp and Cpk indexes are shown in Table 17, where it can be seen that Cp and Cpk values are quite different, indicating that IOH and AC mean are not centered between the limits of the specifications. As mentioned in the Introduction section, the Cp analysis can estimate the proportion of nonconforming product, being desirable to obtain Cp> 1. When obtained Cp> 1, the process can go out of control but still produce conforming items. Analyzing Table 17, it can be seen that it was obtained Cp> 1. Regarding the Cpk, which represents the capability of the process with the existing parameter values, is desirable to obtain Cpk> 1. Analyzing Table 17, it can be seen that it was obtained Cpk <1, which means that the inherent variability in the process, as measured by the process spread 6σ, is greater than the specification spread.

Table 17 – Process capability parameters for the IOH and AC of the RP

Parameter	IOH	AV
Cp	1.259	1.651
Cpk	0.335	0.574

Note: IOH values are acceptable by the customers between 43.5 and 53.5 $mg_{KOH}.g^{-1}$, while AC, acceptable by the customers, are below 3.0 $mg_{KOH}.g^{-1}$, as previously mentioned.

Analyzing the process capability parameters for the IOH and AC of the RP, the RP properties are close to not meeting the customer requirements. This was already

mentioned in the control charts analysis, in which it was discussed some trend and values near the limits. In that sense, corrective actions shall be applied. Possible corrective actions can be identified by numerous tools, such as failure mode and effect analysis (FMEA).

3.3 IMPROVEMENT OF PROCESS QUALITY

A FMEA is an analysis/method to identify potential failure modes and to provide corrective actions. The goal is to define, demonstrate and maximize solutions to attend the safety, quality, reliability, cost or productivity. In that sense, a FMEA was performed to access the quality of RP and the results are presented in Table 18, where it can be observed that potential failure modes associated with the incorrect reaction Temperature and reaction Time were classified with a severity rank of 9. This is due to the fact that the high reaction Temperature or high reaction Time can be extremely dangerous, with potentially hazardous effects. Furthermore, incorrect reaction Temperature and reaction Time can result in the production interruption and damage of the reactor, which ultimately can lead to rework and repairs.

Moreover, despite being classified with a severity rank below 9, the potential failure modes associated with the incorrect amounts of PU and CA showed high RPN values, which, can lead to an unsatisfied customer and to rework and repairs. Also, the use of incorrect amounts of PU and CA can be difficult to detect, so chemical analysis to CA should be carried out. The recommended actions and consequent results are present in Table 19, where it can be seen that, if the recommended actions are taken, the RPN values can be reduced. In other words, the effects of potential failure modes can be minimized, which can improve not only the quality of the RP, but also to improve process safety for workers and equipment.

Table 18 - Process Failure Mode and Effects Analysis (FMEA)

Operation	Description	Potential failure mode	Potential effect(s) of failure	Potential cause(s) of failure	Detection method	Occurrence (O)	Severity (S)	Detection (D)	Risk priority number (RPN)
OP1	Reaction	Incorrect amount of PU	RP with inadequate characteristics	Worker error	Confirmation of the parameter before starting the reaction	4	7	7	196
OP1	Reaction	Incorrect type of PU	RP with inadequate characteristics	Worker error	Operational inspection	4	7	7	196
OP1	Reaction	Incorrect amount of CA	RP with inadequate characteristics	Worker error	Confirmation of the parameter before starting the reaction	4	7	7	196
OP1	Reaction	Incorrect type of CA	RP with inadequate characteristics	Worker error	Operational inspection	4	7	7	196
OP1	Reaction	Incorrect reaction temperature	RP with inadequate characteristics	Worker error	Confirmation of the parameter before starting the reaction	4	9	2	72
OP1	Reaction	Incorrect reaction time	RP with inadequate characteristics	Worker error	Confirmation of the parameter before starting the reaction	4	9	2	72

Table 18 - Process Failure Mode and Effects Analysis (FMEA) (continuing)

Operation	Description	Potential failure mode	Potential effect(s) of failure	Potential cause(s) of failure	Detection method	Occurrence (O)	Severity (S)	Detection (D)	Risk priority number (RPN)
C1	Polyol quality control	Use of incorrect quality control procedures	Incorrect determination of the RP characteristics	Worker error	Measurement of the characteristics of the polyol in triplicate	3	4	3	36
OP1	Reaction	Incorrect amount of PU	RP with inadequate characteristics	Equipment failure	Confirmation of the parameter before starting the reaction	1	7	3	21
OP1	Reaction	Incorrect amount of CA	RP with inadequate characteristics	Equipment failure	Confirmation of the parameter before starting the reaction	1	7	3	21
OP1	Reaction	Incorrect reaction temperature	RP with inadequate characteristics	Equipment failure	Confirmation of the parameter before starting the reaction	1	9	2	18
OP1	Reaction	Incorrect reaction time	RP with inadequate characteristics	Equipment failure	Confirmation of the parameter before starting the reaction	1	9	2	18

Table 18 - Process Failure Mode and Effects Analysis (FMEA) (continuing)

Operation	Description	Potential failure mode	Potential effect(s) of failure	Potential cause(s) of failure	Detection method	Occurrence (O)	Severity (S)	Detection (D)	Risk priority number (RPN)
A1	Storage of raw materials	Incorrect identification of raw materials	Misuse of raw materials	Worker error	Proper separation and identification of raw materials and operational inspection	1	7	1	7
A2	Storage of final product	Incorrect storage of the RP	RP with Inadequate Characteristics	Worker error	Storage of the polyol in closed containers, away from light and moisture	1	4	1	4

Table 19 - Process Failure Mode and Effects Analysis (FMEA) corrected

Operation	Description	Potential failure mode	Potential effect(s) of failure	Potential cause(s) of failure	Detection method	Occurrence (O)	Severity (S)	Detection (D)	Risk priority number (RPN)
OP1	Reaction	Incorrect amount of PU	RP with inadequate characteristics	Equipment failure	Periodic calibration of scales; continuous monitoring of the reaction; double check of the amount weighed	2	4	4	32
OP1	Reaction	Incorrect type of PU	RP with inadequate characteristics	Worker error	Double visual inspection of each batch or raw-materials; continuous monitoring of the reaction;	2	4	4	32
OP1	Reaction	Incorrect amount of CA	RP with inadequate characteristics	Equipment failure	Periodic calibration of scales; continuous monitoring of the reaction; double check of the amount weighed	2	4	4	32
OP1	Reaction	Incorrect type of CA	RP with inadequate characteristics	Worker error	Double visual inspection of each batch or raw-materials; continuous monitoring of the reaction;	2	4	4	32
OP1	Reaction	Incorrect reaction temperature	RP with inadequate characteristics	Worker error	Continuous training of the worker; double confirmation of the reaction temperature	1	4	2	8

Table 19 - Process Failure Mode and Effects Analysis (FMEA) corrected (continuing)

Operation	Description	Potential failure mode	Potential effect(s) of failure	Potential cause(s) of failure	Detection method	Occurrence (O)	Severity (S)	Detection (D)	Risk priority number (RPN)
OP1	Reaction	Incorrect reaction time	RP with inadequate characteristics	Worker error	Continuous training of the worker; double confirmation of the reaction time	1	4	2	8
OP1	Reaction	Incorrect reaction temperature	RP with inadequate characteristics	Equipment failure	Periodic maintenance of the reaction; definition of a limit temperature of reaction	1	4	2	8
OP1	Reaction	Incorrect reaction time	RP with inadequate characteristics	Equipment failure	Periodic maintenance of the reaction; definition of a limit time of reaction	1	4	2	8

CONCLUSIONS AND FUTURE WORK

4 CONCLUSIONS AND FUTURE WORK

The present thesis aimed to optimize, statistically evaluate and contribute to the continuous improvement of a PU recycling method.

A DOE were stablished and the resulting list of experiments was tested. The resulting RP were characterized and the collected data was statistically evaluated using ANOVA and linear regression. The input variables selected are Ratio, Temperature and Time of reaction, while the output variables selected are the IOH and the AC of the resulting RP.

From the ANOVA results, it was observed that Temperature and weight Ratio of PU/CA are the predominant factors which influence the IOH of the RP, having an influence of 62.4% and 31.5%, respectively. Regarding the effect of the reaction conditions on the AC of the RP, distinct results were obtained. The AC is not influenced by a particular factor, instead, it is dependent on several factors and their interactions, being the major influence, the combination of Ratio and Temperature, with a 39.7% of influence. Linear functions of the effect of the reaction conditions on the properties of the RP were also determined using linear regression and despite of the Durbin Watson statistic test and the multicollinearity between IVs results suggest that the linear regression coefficients were poorly estimated, it was observed a high correlation between the experimental and the predicted values.

Afterwards, linear programming was carried out to achieve the best reaction conditions, in which it was found that the RP fulfill the costumer's requirements at the low cost possible. From the results, it was observed that the minimal cost to obtain the RP, attending the properties´ requirements, was 1.1 €.kg^{-1} and to achieve this optimal solution, a Ratio of 5.0, a Temperature of 193.1 ^{o}C and a reaction Time of 4.5 h must be used.

Next, the process control was evaluated using control charts and process capability indexes. From a set of 10 experiments, it was observed that the values of IOH and AC of the RP predominant oscillates randomly around the central line and within the

control limits. However, they also suggest that a cycle may be occurring and that some points are near the control limits. From the Cp and Cpk values, it was confirmed that the IOH and AC mean are not centered between the limits of specifications, being near to not achieve the customer requirements. So corrective actions were identified using a FMEA.

Analyzing the FMEA results, it was observed that the potential failures modes associated with the incorrect reaction Temperature and reaction Time presented high severity. Since if not under control, they can be extremely dangerous, with potentially hazardous effects, which can result in stopping the production, damage the reactor and, ultimately, to rework and repairs. The potential failures modes associated with the incorrect amounts of PU and CA presented as well high RPN values, because can lead to unsatisfied customer and can also stop the production or damage the reactor, leading as well to rework and repairs. In that sense, recommended actions were suggested (such as: periodic calibration of the equipment, continuous training of the workers or special attention paid to the reaction parameter, among others), which, if applied, can reduce the RPN values, thus improving RP quality and process safety for workers and equipment.

For future work, it is suggested to compare the industrial scale results with the pilot scale results. Some deviations may occur due to the scale up and if appropriate, quality tools can be useful for interpreting the results and FMEA can help to identify corrective actions. Moreover, if the industrial scale results do not correlate with the pilot scale results, a new process optimization should be required.

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5 REFERENCES

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APPENDIX

6 APPENDIX I – Production of RP and its characterization

6.1 PRODUCTION OF RP

The recycling of PU wastes consisted in react 1000 g of PU wastes with the proper amount of CA (weight ratios of PU/CA of 4.0 and 5.0), in a 5L Chemglass reactor, under mechanical stirrer and atmosphere pressure. The mixture is heated up to 190 or 200 ^{o}C during 4.5 or 5.5 h. Afterwards, the mixture is cooled to room temperature and the RP is removed from the reactor. In Figure 9, the reactor used and the RP obtained are presented.

(a) (b)

Figure 9 - Image of the reactor used (a) and of the RP obtained (b)

6.2 CHARACTERIZATION OF RP

The acid value (AC) of RP was determined based on ASTM D4662-08 standard (ASTM D4662 - 08, 2008). Approximately 2 g of RP was dispersed in 50 mL of ethanol in a 100 mL Erlenmeyer flask. Titrations were conducted using 0.1 N NaOH solution and the endpoint determined by a digital pH meter (HI 2211 pH/ORP–Hanna Instruments), equipped with a HI 1043B probe. The number of milligrams of KOH required to neutralize the acid of one gram of RP was calculated using equation (22).

$$AC = (A - B) \times 56.1 \times N/W \quad (24)$$

where A is the volume of NaOH solution required for titration of the sample (mL); B is the volume of NaOH solution required for titration of the blank (mL); N is the normality of the NaOH solution; and W is the weight of the sample (g).

The hydroxyl number (IOH) was determined based on ASTM D4274 - 05 standard (ASTM D4274 - 05, 2005) in which the esterification process is catalyzed by imidazole. Titrations were conducted using 0.5 N NaOH solution and the end point determined by a digital pH meter. The IOH was corrected taking into account AV and calculated according to equation (24).

$$IOH = ((A - B) \times 56.1 \times N)/W + AC \quad (25)$$

where A is the volume of NaOH solution required for the titration of the sample (mL); B is the volume of NaOH solution required for the titration of the blank (mL); N is the normality of the NaOH solution; W is the weight of the sample (g); and AC is the acidity of the sample ($mg_{KOH}.g^{-1}$).

7 APPENDIX II – Determination of the process costs

For the determination of the total costs of the process, was taken into account two types of costs:

- The cost associated with the reactants (Reactant cost);
- The cost associated with the reaction (Energy cost).

Regarding the reactants cost, accordingly with industrial partners, the price of PU wastes is 0.4 €.kg^{-1}, while the price of CA is 1.6 €.kg^{-1} and determined by:

$$Reactant\ cost(€) = m_{PU} \times price_{PU} + m_{CA} \times price_{CA} \quad (26)$$

where m_{PU} it the mass of PU (kg) and m_{CA} is the mass of CA (kg) used in the reaction.

In Table 20, it is listed the cost of each Ratio used.

Table 20 - Contribution of reactants to the process cost

Ratio	PU (kg)	CA (kg)	Cost (€.kg^{-1})
4.0	0.75	0.25	0.70
4.1	0.76	0.24	0.69
4.2	0.76	0.24	0.69
4.3	0.77	0.23	0.68
4.4	0.77	0.23	0.67
4.5	0.78	0.22	0.67
4.6	0.78	0.22	0.66
4.7	0.79	0.21	0.66
4.8	0.79	0.21	0.65
4.9	0.80	0.20	0.64
5.0	0.80	0.20	0.64

The results presented in Table 20 were used to determine the relationship between the cost of reactants and the Ratio, using linear regression. The data was computed using the IBM SPSS 25 software and the result are presented in Figure 10.

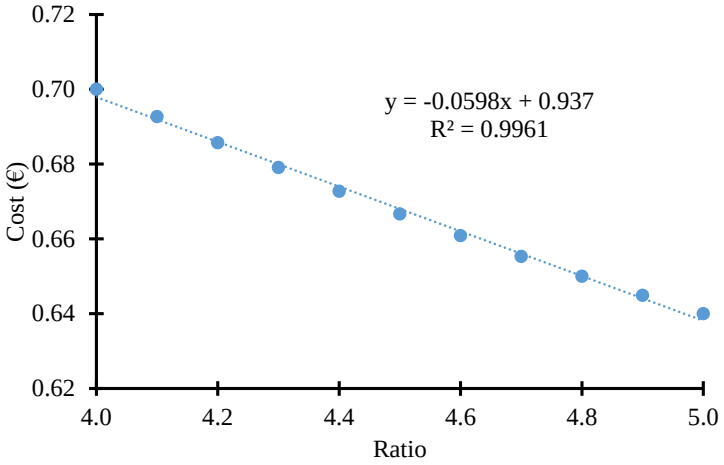

Figure 10 - Effect of ratio on the process cost

From Figure 10, it can be stablished that the relationship between the cost of reactants and the Ratio is:

$$Reactant\ cost(€) = -0.060 \times Ratio + 0.937 \quad (27)$$

For the determination of the costs associated with the reaction, was taken into account two variables:

- The energy consumption for each degree Celsius (°C);
- The energy consumption for each hour (h) of reaction.

First, it was measured the energy consumption of the reactor for different temperatures during 1 h and results are presented in Table 21.

Table 21 - Energy consumption of reactor measured

Temperature (°C)	Time (h)	Energy ($kW.h^{-1}$)
190	1	0.806
195	1	0.910
200	1	0.935

Next, it was estimated the energy consumption of the reactor for different temperatures, during different times and the associated costs were determined.

$$Energy\ cost(€) = Cost_{temperarture\ X} \times hours \quad (28)$$

where, $Cost_{temperature\ X}$ is the energy cost of maintain the reactor at 190, 195 or 200 °C (see Table 21) and the *hours* is the number of hours that the reactor has been operating. The corresponding results are presented in Table 22, which were then used to establish the relationship between the cost of reaction and the reaction conditions, using linear regression.

Table 22 – Estimation of energy consumption cost of reactor

Temperature	Time	Energy consumption (kW)	Cost (€)
190	4.5	3.6	0.36
195	4.5	4.1	0.41
200	4.5	4.2	0.42
190	5.0	4.0	0.40
195	5.0	4.6	0.46
200	5.0	4.7	0.47
190	5.5	4.4	0.44
195	5.5	5.0	0.50
200	5.5	5.1	0.51

Note: accordingly to industrial partners the price of one KW is 0.1 €

The data was computed using the IBM SPSS 25 software and the results are presented in Table 23.

Table 23 – Linear regression coefficients for the effect of the reaction conditions on the process cost

Constant	-1.292
Temperature (°C)	0.007
Time (h)	0.087

From the results presented in Table 23, it can be stablished that the relationship between the cost of the reaction and the temperature and time of reaction is:

$$Energy\ cost(€) = -1.292 + 0.007 \times Temperature + 0.087 \times Time \quad (29)$$

Finally, the total costs of the process can be determined by:

$$Total\ cost(€) = Reactant\ cost + Energy\ cost \quad (30)$$
$$= -0.060 \times Ratio + 0.937 - 1.292 + 0.007 \times Temperature + 0.087 \times Time$$
$$= -1.352 - 0.060 \times Ratio + 0.007 \times Temperature + 0.087 \times Time$$