Design of Experiments (DOE) for Product and Process Improvements: A Phenolic Syntan Case Study

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Abstract. For sustainable developments the chemical industry is continuously looking for technical innovations with wide potential implications. The Design of Experiments (DOE) approach has been proven to be a powerful tool in determining the relationship between factors affecting output variables. DOE is done to identify the first order effects and higher order interactions and eventually realize output optimization. Although we can influence properties by application, the effect a retanning agent has on leather originates to a large extent from the chemistry involved. To understand interactions and the possibilities of targeted improvements of the production process, a DOE factorial design approach was used to identify the control parameters and their interactions in our phenolic syntan recipes. Instead of trial-and-error or one-factor-at-a-time practices, DOE made it possible to limit the number of lab experiments and still quantify the first order effects and the higher order interactions. As a result, a much deeper and more consistent understanding of the building blocks' interactions and how these influence the chemical process of phenolic syntan synthesis has been gained. This includes the amount of different building blocks, their molar ratios as well as process conditions. Aiming at achieving optimal efficiency for various projects, right now we are looking at possibilities in implementing DOE within Smit & zoon.

1 Introduction

The production of chemical ingredients can be described by a process of multiple factors for example molar ratios of different raw materials and process conditions such as temperatures, pressure, stirring speed and process time. This process creates all kinds of measurable data labelled as response information (see figure 1). Using Design of Experiments (DOE) the impact of multiple factors on a response can be investigated by simultaneously adjusting levels of multiple factors in each test run. To optimize the process on a response, it is important to obtain the right factors and the interaction of different factors having their effect on a certain response.

Figure 1. Process overview from factors to responses.

A specific process is the production of a group of re-tanning agents which are so-called phenolic resins. These widely known polymer products are for instance produced by a condensation reaction of phenol-sulphonic acid with formaldehyde together with other building blocks like other aromatics or amines.

This article describes the case study of a small DOE model for obtaining control factors and interactions on the response of free phenol content in powder products.

2 Materials and Methods

2.1 Materials

Chemicals used for the analysis of free phenol are purchased from different lab chemical suppliers such as Sigma Aldrich (phenol ≥99%), Acros Chemicals (4-aminoantipyrine 98%) and Chem-Lab (potassiumhexacyanoferrate [III] p.a.). For the synthesis of a phenolic resin, chemicals like acids, caustic, aldehyde solutions, aryl- and amine compounds are used from own production stocks.

2.2 Analytical method to analyze phenol content

Emerson's reagent (4-aminoantipyrine – potassiumhexacyanoferrate [III]) is widely used for the determination of phenol. In this method the free phenols are released when syntan are dissolved and separated from interfering constituents by steam distillation. The phenolic compounds are buffered to a pH of 10 in order to prevent formation of quinonoid substitution products (antipyrine red). The free phenol present in the aqueous solution is then reacted with Emerson's reagent [1] to form a yellow-red complex, depending on amount of reacted phenol. This complex can then be quantitatively determined via spectrometry. Emerson's reaction has many advantages: speedy results, easy manipulation, use of stable reagents, applicability over a wide range of concentration of phenolic materials [1].

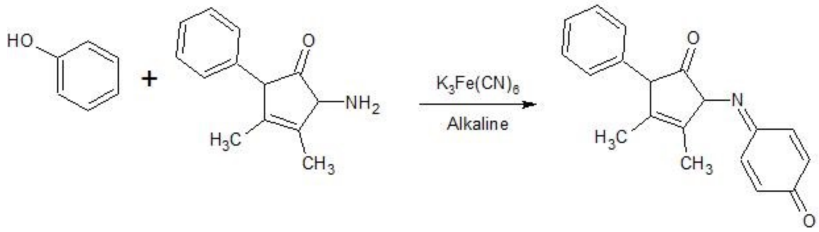

Figure 2. Emerson's reagent reaction with phenol

2.3 Full factorial design

The experiment is set up by using a full factorial design where three factors (A, B and C) will be investigated (see figure 3). Each factor will have an upper and a lower value (blue balls) and an additional experiment in the center of these factor settings (green ball). This center point helps to see whether the interactions between the factors are linear or not.

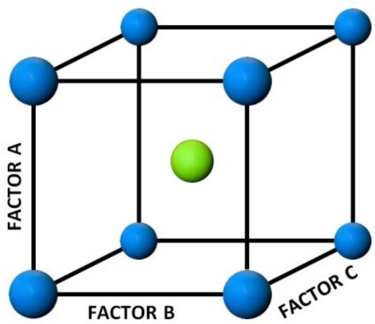

Figure 3. Cubic plot of factors with a center point in a full factorial design set up.

In table 1, an overview of 9 experiments is shown for the design set up in this study. Factor A and B are of chemical origin and factor C being a technical one.

Table 1. Expression of corner and center points of a cubic plot

Experiment	Setting Factor A	Setting Factor B	Setting Factor C
1	High	High	High
2	High	High	Low
3	High	Low	High
4	High	Low	Low
5	Medium	Medium	Medium
6	Low	High	High
7	Low	High	Low
8	Low	Low	High
9	Low	Low	Low

2.4 Preparation of a re-tanning agent

As an example for the investigation, a simple process for the synthesis of phenolic resins is used, comparable to the example used by E. Stiasny [2]. For the equipment a 2 ltr, three-necked round bottom flask with condenser and dropping funnel is used including stirring and thermometer. The first step in the reaction process is the sulphonation of phenol at 100°C, followed by the addition of water and an amine, like urea. At 65°C the condensation reaction with an aldehyde takes place. After this step the reaction mixture is partially neutralized. A second addition of phenol and aldehyde was used to continue the polymerization. Finally, the product was finalized by setting a required pH with sodium hydroxide. The liquid product is spray dried into a powder version by using a pilot spray dryer (Anhydro Lab 1). This product is analyzed on the amount of free phenol.

3 Results and Discussion

All nine syntheses resulted in powder products that made it possible to analyze their free phenol content in ppm (see table 2). This design inputs have been entered in the powerful calculation tool MiniTab®18 [3].

Table 2. Data overview of factors, level settings and response.

Experiment	Setting Factor A	Setting Factor B	Setting Factor C	Response Phenol content
1	0.09	2.00	120	< 50
2	0.09	2.00	15	601
3	0.09	1.25	120	2060
4	0.09	1.25	15	7047
5	0.045	1.63	68	1274
6	0	2.00	120	< 50
7	0	2.00	15	655
8	0	1.25	120	1800
9	0	1.25	15	6041

To show the effect of each factor, the average response of each low and high level factor is calculated for that specific factor (see figure 4). A large slope corresponds to a strong effect caused by that factor. When the graph has a small slope, or even a horizontal line, the effect is getting more and more negligible. From this graph it can be seen that factor B and C have a strong effect, while the response effect for factor A is almost negligible for the selected levels.

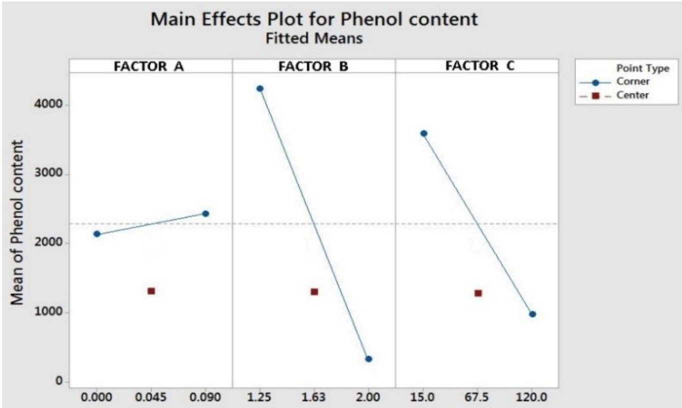

Figure 4. The effect of a single factor on the response.

In this design, there are three two-factor interactions, so-called 2nd order interactions, namely AB, AC and BC. For these interactions, it is also possible to calculate the effect of these factor-interactions, visualized in figure 5. When lines are parallel to each other, there is no interaction between two factors and therefore no additional effect. There is an interaction when lines will attend to cross each other, for example as for factor B with C, causing an additional effect on the response.

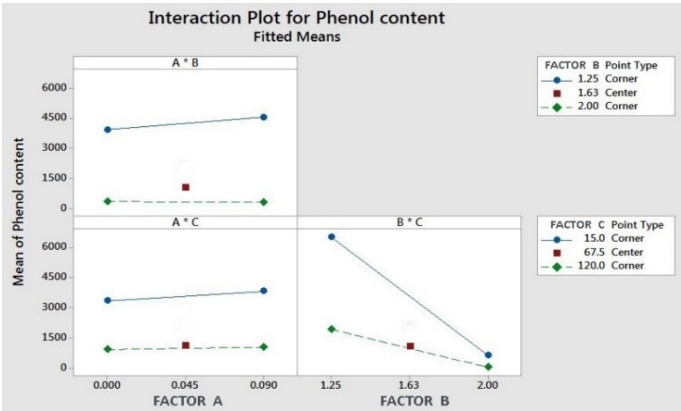

Figure 5. Interaction plot of different factors on response.

Besides the factors themselves and the 2nd order interactions, there is also a 3rd order interaction, mentioned as interaction ABC. The effect is calculated in the same way like the 2nd order interaction. To visualize the magnitude and the importance of all the effects from largest to smallest, a Pareto chart is made (see figure 6). In this case it is clear that factor B and C and the 2nd order interaction BC have the highest effect. The 3rd order interaction ABC is almost negligible in this case study.

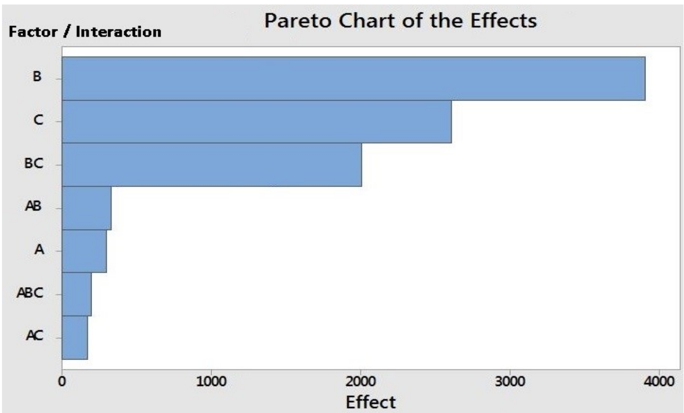

Figure 6. Effect impact for each factor and interaction

4 Conclusion

Design of Experiments (DOE) has been proven to be efficient and effective in product and process improvement in a phenolic syntan case study. From this case study, it is thought that decreasing the amount of free phenol in the product is possible, by increasing factor B and factor C within the recipe. The interaction of both factors (BC) even strengthens the effect. Factor A does not have a significant impact on the response, nor its interaction with other factors.

5 Outlook

DOE factorial design can be used to identify factors (control parameters) and especially their multiple order interactions in a wide range of (industrial) applications. The approach of large systems, high amount of factors, by using DOE is an effective and efficient way to obtain that knowledge. Increasing the amount of factors increases the amount of experiments tremendously, according to equation (1);

$$L^k = number\ of\ experiments \quad (1)$$

L is the number of levels for each factor
k is the number of different factors

In table 3 an overview is shown on the number of experiments required for the amount of factors in a 2-level system. Depending on the resources available, the amount of experiments can be reduced using fractional factorial design. This leaves out the highest order interactions, because the change of a big impact on the response is small. For that reason, the amount of experiments can be significantly reduced, while obtaining great amount of knowledge of factor and lower order interaction effects.

Table 3. Factorial designs in a 2-level system

	Factors								
# exp	2	3	4	5	6	7	8	9	10
4	Full	n.a.	n.a.						
8		Full	Fract	n.a.	n.a.	n.a.	n.a.		
16			Full	Fract	Fract	Fract	Fract	n.a.	n.a.
32				Full	Fract	Fract	Fract	Fract	Fract
64					Full	Fract	Fract	Fract	Fract
128						Full	Fract	Fract	Fract

Full: full factorial design, maximum of information (green)
Fract: fractional factorial design, high degree (green) or less degree (yellow) of information
n.a.: not applicable, too much loss of information (red)

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