Optimization of the Process of Melana Fibres Dyeing with Methylene Blue in the Presence of Maleic Copolymers

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In this paper, data on Melana-type polyacrylonitrile fibers dyeing with Methylene Blue in the presence of maleic acid copolymers with vinyl acetate or styrene are presented. Mathematical models of the studied dyeing processes have been developed and the necessary information on their significant factors are produced by means of experiment planning methods, known as Design of Experiment (DoE) or Experimental design. Optimal correlations between the application conditions and the color differences obtained on Melana fiber type have also been studied.

Keywords: polyacrylonitrile fibers, dyeing, maleic acid copolymers, Methylene Blue, methods of planning experiments (DoE), color differences

There are several studies concerning the processes of textile material dyeing with anionic dyes using cationic equalizers, but in the case of textile material dyeing with cationic dyers that use as retarders the anionic compound based on polyelectrolyte, there are very few references in literature [1-3].

The affinity of cationic dyestuffs for acrylic fibres is high, due both to the electrostatic attraction and the hydrophobic interactions between fibre and dyestuff, which involves production of non-uniform dyeing for acrylic fibres [2, 4-6].

The present study pursues the influence of concentration of polyelectrolyte and dyestuff, as well as of dyeing duration or temperature on the colour difference y or (ΔE), at Melana type poly-acrylonitrile fibres. The optimum correlation between the application conditions and the colour differences in the Melana fibres have been studied using mathematical modelling elements, in view of industrial application of polyelectrolytes based on anionic maleic copolymers.

Experimental part

Materials and methods

Dye: was the Merck reactive Methylene Blue (MB) used as received, without purification or other modifications. The dye structure is presented in figure 1.

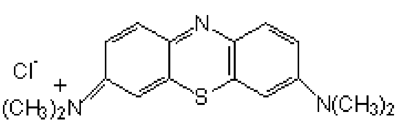

Fig. 1. Chemical structure of the Methylene Blue dye

Polyelectrolytes: was a copolymer of the maleic acid with vinyl acetate (NaM-VA) (a) and a copolymer of the maleic acid with styrene (NaM-S) (b), both in the state of natrium salts. The two copolymers were obtained from the copolymer of the maleic acid with vinyl acetate or styrene, synthetized according to a method described in literature [7, 8]. The chemical structures of the polyelectrolytes are presented in figure 2.

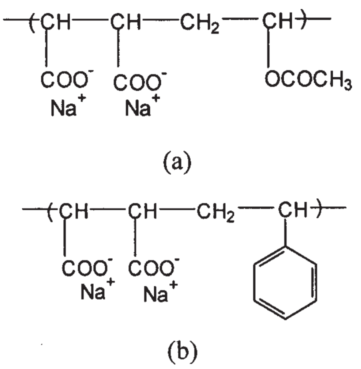

Fig. 2. Chemical structures of the copolymers natrium maleate with vinyl acetate (NaM-VA) (a) and natrium maleate- styrene (NaM-S) (b)

Melana Fibre: The Melana Fibre is a polyacrylonitrile fibre based on a ternary polymer (acrylonitrile, vinyl acetate, α-methylstyrene) obtained through a radical polymerization reaction initiated in the redox system with potassium persulphate - natrium metabisulphite.

Dyeing Procedure. The dyeing process was performed on a Mesdan Lab dyeing device with six dyeing positions. Melana fibres dyeings (by six dyeing operations of 1.0g sample for each colour position) in aqueous solutions (distilled water) of MB in the presence of the polyelectrolytes NaM-VA or NaM-S, at dye and polyelectrolyte concentrations of 0.5; 1.0; 1.5; 2.0 and 2.5, at a *p*H of 5.5-6, with 10% acetic acid and a liquor ratio of 1:50. Practically, in the aqueous solution of dye, polyelectrolyte in different concentrations is added and a few drops of acetic acid are added to adjust the *p*H. The dyeing flask is magnetically stirred for 5 min for homogenization, then the solution is kept still for 30 min, after which the Melana fibres (1.0g) are introduced in the solution. The solution is stirred again for 5 min, then the dyeing flask is subject to the following thermal regime: the dyeing liquor is heated up to 80°C, which is maintained for 10 min. Then the heating continues up to temperatures of 85, 90, 95 or 100°C, at a

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Factor	UM	coded factor	$x_{min} \to x_{max}$	x_{io}	-2	-1	0	1	2	Var. step
Dye concentr.	%	x_1	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Polyelectrolyte concentration	%	x_2	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Dyeing time	min	x_3	30→120	75	30	52.5	75	97.5	120	22.5
Dyeing temperature	°C	x_4	80→100	90	80	85	90	95	100	5

Table 1
FIELDS AND STEPS OF VARIATION FOR INDEPENDENT VARIABLES

rate of 1°C/min, the temperature being maintained for about 10 min , after which the dyeing solution is slowly cooled down. The dyed Melana is intensely washed for 5 min with cold and hot water respectively, squeezed by hand and dried at room temperature.

Colour differences have been measured with a portable Datacolor 2002 spectrophotometer type Check Plus [2, 9-17].

In order to obtain the mathematical model of the studied processes and the necessary information on the significant factors, the experiment planning is carried out, known as *Experimental design or Design of Experiment* (*DoE*) [2, 18].

The data collected according to the experimental program are used to estimate the model coefficients. These represent the relation between the response y (ΔE) and the factors x_1, x_2 ... x_n. The principle of the estimation (approximation) method is represented by the multiple linear regressions (RLM) [2,19].

Experimental design is a branch of the mathematical statistics and includes the mathematical tools used to establish the number of experiments, the conditions of realization and the methods to estimate the experimental results [2, 18-20]

The adequate experimentation project is chosen in terms of the type of the necessary dependence. *The central rotable composed programs* are the most indicated for the type of problem approached in this study. We mean to obtain minimum dispersions, equal in all the experimental points. The experimental points must be situated at approximately equal distances to the program centre, in order to realize equal dispersions.

The central rotable composed program for four independent variables contains 31 experiments [2]:

- 16 experiments corresponding to the program 2^4;
- 7 experiments situated on the axes of coordinates at distances $\alpha = \pm 1$;
- 7 experiments in the program centre.

In the present case we performed 31 dyeings for each of the 2 systems.

Optimization Method

In this case the *Method of descending simplex* is used [2]. This differs from other deterministic minimization methods because it does not explicitly need one-dimensional optimization algorithms [2, 21]. The method presents the evaluation principles only for functions, not for the derivatives, being a 0th order method [2, 22].

Based on experimental results and theoretical appreciations concerning the Melana fibres dyeing process with cationic dyestuffs in the presence of anionic polyelectrolytes, the colour modifications y_e (ΔE) were chosen as optimization criterion [2, 23]. The factors (independent variables) with significant influence on the process have been established, namely x_1- dyestuff concentration (%), x_2 – polyelectrolyte concentration (%), x_3 – dyeing time (min) and x_4 – dyeing temperature (°C) [2].

Within the statistical modelling, the determination fields of the experiment centre and the variation step have been established for each factor apart, taking into account the restrictions for the technological and technical realization of the process. The data are illustrated in table 1.

The study was performed on the three mentioned dyestuffs applied through a dyeing procedure through depletion.

Results and discussions

The data collected according to the experimental program are used to estimate the model coefficients. This represents the relationship between the responses *ye* (ΔE) and the factors x_1, x_2, x_3 and x_4.

Based on the results provided by the MODDE program, it has been considered that the equation which expresses the best ye(x_1, x_2, x_3, x_4) has the form:

$$ye = bo + b_1x_1 + b_2x_1 + b_3x_3 + b_4x_4 + b_{11}x_1{}^2 + b_{22}x_2{}^2 + b_{33}x_3{}^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4$$

After this, a statistic model was elaborated through a *central rotable composed program for four independent variables.*

Based on the experimental program and experimental results produced through automated processing on an IBM-PC computer, the response functions for the three studied dyestuffs are presented bellow [2].

Tinctorial Systems: Melana fibre dyed with MB in the presence of NaM-S or NaM-VA

Based on the results of the performed experiments, we have obtained for the tinctorial system (MB, NaM-VA, Melana) the following mathematical model:

$$\begin{aligned} ye &= 13.72 + 2.4325x_1 + 1.75667x_2 + 1.805x_3 - \\ &- 2.3825x_4 - 1.41771x_1^2 - 1.79021x_2^2 - 1.91896x_3^2 \\ &- 2.48396x_4^2 + 2.12x_1x_2 + 0.79125x_2x_4 - 1.195x_3x_4 \end{aligned}$$

After examining the coefficients of the mathematical model within the field of the established factors, the following information was obtained:

- colour difference (*y*) increases with increasing concentration of the dyestuff MB (x_1), and the polyeletrolyte NaM-VA (x_2), and the dyeing time (x_3) and it decreases with increasing dyeing temperature (x_4).
- y_e decreases with the increase of the values of $x_1{}^2$, $x_2{}^2$, $x_3{}^2$ and $x_4{}^2$;
- y_e increases with the increase of the values of x_1x_3 and x_2x_4 and decreases with the increase of x_3x_4.

The results of a previous study [2] concerning Melana fibres dyeing with MB in the presence of NaM-VA have shown that ΔE increases within the range 11.5→ 12.3 (AN) with the increase of the NaM-VA concentration from 0→ 2.5% in the dye liquor, and it increases from 11.2→14.1 (AN) with the increase of the dyeing time from 30 to 120 min. At the same time, ΔE decreases (15.08→8.35) (AN) with increase of the dyeing temperature within the interval 80→100°C.

The absorption of the cationic dyestuffs by the polyacrylonitrile fibres follows an isotherm with saturation limit of Langmuir one. Starting from the modified equation of Langmuir isotherm and using the classical Donnan models or the modified Donnan model, several authors have shown that dyeing the acrylic fibres with cationic dyestuffs can be explained through an ionic and hydrophobic exchange between the fibre and the dyestuff [2].

Dyeing of polyacrylonitrile fibres with cationic dyes occurs in three stages:

- adsorption of dyes cation on the fibre external surface;
- dyes diffusion inside the fibre;
- generation of electrovalences between the dyes cations and fibre anions.

The first and the third stages occur with very high velocities, while the velocity of the second stage is determined for the entire dyeing process.

The factors which govern the first stage are the temperature, dyeing liquor stirring and the fibre electric potential.

A static laminar boundary bath layer is formed around the acrylic fibre, whose thickness changes in inverse ratio to the velocity of dye liquor flowing around the fibre; due to diffusion, the dyestuff molecules cross at first this layer and then reach the fibre surface [2, 24]. Once at the surface, the cationic dye diffuses inside the fibre, making possible the dye depletion from the dye liquor; the spots on the fibre external surface, left free due to diffusion toward the inside the fibrous polymer remain vacant and will be later on occupied by other dyestuff molecules from the dye liquor.

The diffusion stage is the slowest, influencing the dyeing rate. Both the dyestuff diffusion and the dyeing rate are influenced by temperature.

During the dyeing process, the dyestuff can be easily released and absorbed on the textile substrate due to the generation of the new compound. The anionic retarders interact with dyestuffs, forming a compound with a smaller diffusion velocity inside the solution, therefore a slower sorption. The mechanism of dyestuff bonding to the PAN fibre in retarder presence can be schematically represented as follows [2]:

$$\mathrm{Col^{+} + Ret^{-}} \underset{>80^{\circ}\mathrm{C}}{\overset{<65^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{Col - Ret}$$

$$\mathrm{Col^{+} + PAN^{-}} \underset{>95^{\circ}\mathrm{C}}{\overset{>65^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{Col - PAN}$$

where Col^+ – dyestuff cation; Ret^- – retarder (polyelectrolyte) anion; PAN^- - free anionic groups from the ends of polyacrylonitrile macromolecular chains.

The presence of the NaM-VA polyelectrolyte in the dyeing system determines a process of acceleration of Melana sample dyeing with MB irrespective of concentration, due to the hydrophilic character and the absence of the steric hindrance phenomenon which determines a quick release of the dye cations. The effect of acceleration of Melana fibre dyeing with MB in the presence of NaM-VA is determined by the easiness with which the dye cations are released from the metachromatic compound and by the accessibility to react with the anionic groups from the ends of Melana fibre chains [2, 24].

The previous communications [2] justify the mathematical model obtained for the tinctorial system: MB dyestuff, NaM-VA polyelectrolyte and Melana fibres.

Based on the results of the performed experiments, the following mathematical model was obtained for the (MB, NaM-S, Melana) tinctorial system:

$$\begin{aligned} ye &= 8.87 + 3.17625x_1 - 2.29875x_2 + 1.43542x_3 + \\ &+ 1.17542x_4 + 0.939837x_2^2 - 0.726413x_3^2 \\ &- 0.871413x_4^2 - 0.813125x_1x_4 - 0.849374x_2x_4 + 1.51813x_3x_4 \end{aligned}$$

By examining the coefficients of the mathematical model within the range of the values of the considered factors, the following information was obtained:

- the colour difference *y* increases mainly with the increase of the dye concentration (x_1), dyeing time (x_3) and temperature (x_4), and it decreases with the increase of the polyelectrolyte concentration (x_2);
- y_e increases with the increase of x_2^2 values and decreases with the increase of x_3^2 and x_4^2 values;
- y_e increases with the increase of x_3x_4 and decreases with increasing x_1x_4, x_2x_4.

The increase of the dyeing temperature results in colour modifications of the Melana samples dyed with MB in the presence of the two polyelectrolytes, fact revealed by the values of the colour difference ΔE. For instance, at the maximum dyeing temperature of 100°C, the colour differences are minimum (8.05 AN) in the case of (Melana, MB, NaM-VA) system. When the dyeing temperature decreases to the minimum value of 80°C, the value of the colour difference ΔE is maximum (15.02 AN). In the case of the (Melana, MB, NaM-VA) system, the maximum colour difference is obtained at the temperature of 90°C. Based on the chromatic values obtained in previous studies, the temperature is considered as a determinant factor for these tinctorial systems [2].

When adding NaM-S in the dyeing solution, the colour difference modifies: at small NaM-VA concentrations, the MB aggregates from the solution break off, part of dye ions interact with the polyelectrolyte charged positions and others with the anionic positions from the ends of the Melana fibre, establishing ionic bonds. When the NaM-VA concentration in the dye liquor increases, the hydrophobia and the steric hindrance due to the styrene rest increases, resulting in the retardation or even blockage of the molecules or „small" dye aggregates migration toward the charged position from the Melana fibre chains ends. In these cases, the amount of dye fixed on Melana fibres is small, and the dyeing becomes non-uniform, a colour aspect visually confirmed.

The polyacrylonitrile fibres are hydrophobic, the water sorption under standard conditions being of 1-2%, and swelling in water is especially small [3, 4].

Recent studies of spectral remission show that at small NaM-S concentrations (0.5%), an acceleration of Melana fibre dyeing with MB occurs, but when the polyelectrolyte concentration in the dye liquor increases (1.5-2.5%) the retardation of Melana fibres dyeing occurs [2].

In other words, when the dye liquor temperature increases, Melana quite quickly depletes the dyestuff, as the cationic dye is rapidly absorbed by the fibre. In order to retard the absorption, a retarder is added in the dye liquor, which is depleted faster than the dye on the fibre, resulting in a slower and more uniform passage of the dye cation on the fibre [2].

The possible interactions between the partners from the dye liquor determine the generation of a complex

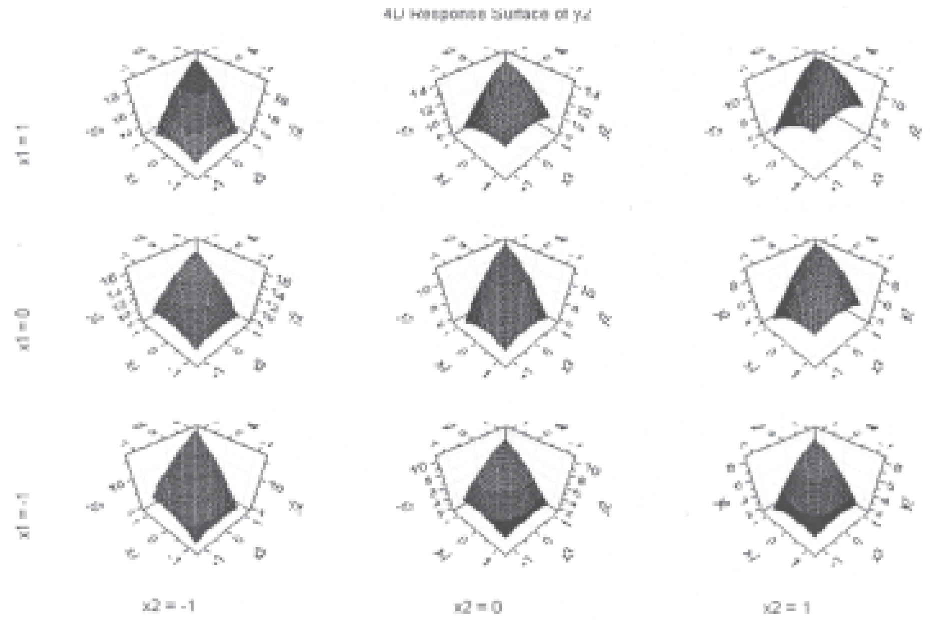

Fig. 3. Response surfaces for Melana fibre dyed with MB in the presence of NaM-S

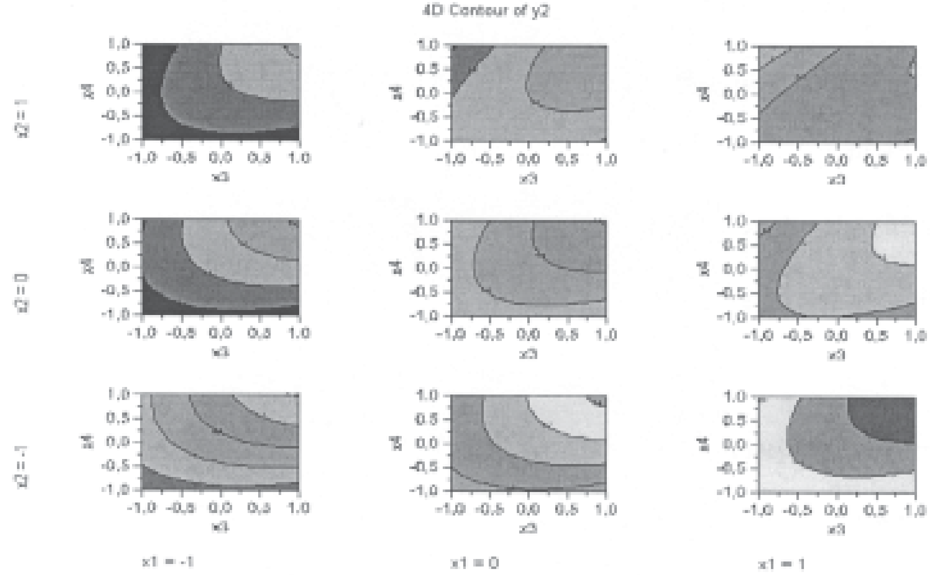

Fig. 4. Level curves for Melana fibre dyed with MB in the presence of NaM-S

system, hard to detect through known investigation means, and this in the situation when the highest weight belongs to the electrostatic and hydrophobic interactions in the tinctorial system. Depending on the thermal regime, duration, chemical and structural characteristics of the partners, as well as their concentration, the polyelectrolytes presence can result in either acceleration or retardation of dyeing.

Mathematical models presented here were subsequently used to predict the studied processes and to determine the processing conditions necessary for optimal governing.

In order to predict the influence of the independent variables on y_e (ΔE) and their interactions, 234 response surfaces and 207 level curves were mapped out for the 2 studied systems. Each time two factors were maintained constant (x_1, x_2 coded, equal to -1, 0 or 1), the other three being modified (fig. 3 and 4) [2].

In the present case, we expose for illustration the response surfaces and the level curves for Melana fibre dyed with MB in the presence of NaM-S when the concentration of the dye (x_1) and polyelectrolyte (x_2), as well as the dyeing duration (x_3) change, while the dyeing temperature (x_4) is kept constant [2].

The obtained response surfaces are types of ascending ridge, oblong saddle or, elliptic valley while the level curves are constantly hyperbolas, ellipses or parabolas with saddle points for some systems, that can be displaced toward the y (ΔE) maximum value, and maximum or minimum points in certain cases [2].

The problem of optimization tackled here is a problem maximization of colour difference y_e (ΔE), its solution being obtained in the MODDE application with descending simplex [2].

Optimization of the process of Melana fibres dyeing with MB in NaM-VA presence

The optimization of the process of Melana fibres dyeing with MB in NaM-VA presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 2.

Under these conditions, the optimum value of the colour difference is $y_{e1} = 18.9002$ and the values obtained for the deciding variables are: $x_1 = 2.5$, $x_2 = 2.2532$, $x_3 = 90.4014$, $x_4 = 87.110$ corresponding to the coded values 2; 1.5045; 0.6412 and 0.4101 respectively.

Finally, experimental verification of the found optimum values was performed. With this aim in view, the decisive variables were established at the obtained values. After the experiment, the measured value of y_e was 18.54, which confirm the estimated optimums.

Table 2
MAXIMUM VALUES OF THE COLOUR DIFFERENCE

No.	x_1	x_2	x_3	x_4	y	iter	log (D)
1	1.9966	1.5251	0.6751	0.4462	18.9116	0	-10
2	1.9974	1.529	0.694	0.473	18.9091	0	-10
3	2	1.4251	0.6516	0.4972	18.8851	0	-10
4	**2**	**1.5045**	**0.6412**	**0.4101**	**18.9002**	**0**	**-10**
5	1.9977	1.5233	0.7113	0.4593	18.9106	0	-10
6	1.8	1	1	-1	18.0087	0	-2.682
7	1.9977	1.5233	0.7113	0.4593	18.9106	0	-10
8	1.9977	1.5233	0.7113	0.4593	18.9106	0	-10

Table 3
MAXIMUM VALUES OF THE COLOUR DIFFERENCE

No.	x_1	x_2	x_3	x_4	y	iter	log (D)
1	1.9504	-2	0.7894	1.9966	29.1199	0	-10
2	-2	-2	0.8	2	19.6604	16	-10
3	2	-2	0	-2	21.3733	6	-10
4	1.9997	-1.9979	0.2366	0.0099	27.585	0	-10
5	**1.9801**	**-1.9823**	**1.4781**	**1.0874**	**29.9017**	**0**	**-10**
6	1.8	-1	1	1	21.852	0	-10
7	1.9999	0.6002	1.9998	1.4918	21.3465	123	-10

Optimization of the process of Melana fibre dyeing with MB in NaM-S presence

The optimization of the process of Melana fibres dyeing with MB in NaM-S presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 3.

Under these conditions, the optimum value of the colour difference is of y_{e1} = 29.9017 and the optimum values of the deciding variables are: x_1 = 2.49955 g/l, x_2 = 0.549965 g/l, x_3 = 110.96175 min, x_4=95.4735°C corresponding to the coded values 1.9801; -1.9823; 1.4781 and 1.0874 respectively.

Finally, experimental verification of the determined optimum was performed. With this aim in view, the deciding variables were fixed at the obtained values. As the result of the experiments, the measured value of y_e was of 30.12, which confirms the estimated result.

Conclusions

From the examination of the mathematical model coefficients within the fields of the values of the considered factors for the six systems, one can notice that the colour difference ΔE is mainly influenced by the four independent variables: dye concentration, polyelectrolyte concentration, dyeing time and temperature.

The response surfaces are of the type ascending ridge, oblong saddle or elliptical valley, while the level curves are hyperbolas, parabolas or ellipses, with the saddle point for some systems which can be displaced toward the maximum value of y (ΔE), as well as maximum or minimum points in certain cases. There are also situations where straight lines appear which indicates the insignificant influence of some parameters on the target function.

The optimization of the processes of Melana fibers dyeing with MB in the presence of maleic polyelectrolytes with vinyl acetate NaM-VA or styrene NaM-S was performed without starting values, when these are implicitely generated by the *MODDE* application. It was found out that the y_e values measured during the experiments performed for the two systems are close to the y_e optimum estimated values.

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