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Supporting Information

Modelling of the Effect of Concentrated Nitration Conditions on the Efficiency of the Production of 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)

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Table S1. Melting point of DPT, RDX and HMX

Material	melting point (°C)
DPT	201-205
RDX	205.5
HMX	276-286

Table S2. Data of chromatograms obtained for DPT containing HMX and α-HMX

The chromatogram obtained for DPT (28.3979 g) containing HMX (0.0156 g) (Figure 6S)		
Region	Retention time (min)	related to
1	2.52	solvent used
2	4.15	DPT
3	5.19	HMX impurity
The chromatogram obtained for DPT (28.3979 g) containing α-HMX (0.0275 g) (Figure 7S)		
Region	Retention time (min)	related to
1	4.95	DPT
2	5.37	α-HMX
3	9.28	RDX impurity

Table S3. The process parameters and their chosen levels

Parameters	Notation	Levels				
		-2	-1	0	1	2
volume of ammonium nitrate–nitric acid solution (mL)		20	25	30	35	40
nitration temperature (°C)		32	39	46	53	60
time of adding to the reactor (min)		15	18.75	22.50	26.25	30
volume of acetic anhydride (mL)		60	65	70	75	80

Table S4. Design of experiment (DOE) and the results of it

Run order	Input parameters				Responses	
	x_1 (mL)	x_2 (°C)	x_3 (min)	x_4 (mL)	Pr (100 g · mL^{-1})	E (%)
1	35	53	18.75	75	12.17	40.09
2	25	39	26.25	75	11.00	34.22
3	25	53	18.75	65	16.90	59.41
4	25	39	18.75	75	12.56	51.51
5	25	39	26.25	65	15.11	44.18
6	35	39	26.25	75	12.16	53.06
7	25	53	26.25	75	16.32	50.75
8	25	53	18.75	75	18.69	58.10
9	30	46	22.50	70	19.94	47.99
10	35	39	18.75	75	12.74	41.96
11	30	46	30.00	70	20.77[a]	64.58[b]
12	30	46	22.50	70	20.13	48.58
13	30	46	22.50	70	20.09	48.47
14	30	46	22.50	70	20.22	48.88
15	35	53	26.25	75	12.58	41.47
16	30	46	22.50	70	19.95	48.05
17	20	46	22.50	70	14.96	43.75
18	30	46	15.00	70	19.51	60.67
19	35	53	18.75	65	12.25	38.09
20	40	46	22.50	70	11.40	37.57
21	30	46	22.50	70	20.01	62.21
22	30	46	22.50	80	14.66	48.31
23	30	60	22.50	70	15.58	48.45
24	35	39	26.25	65	15.52	48.25
25	30	46	22.50	60	16.46	48.12
26	30	46	22.50	70	20.05	62.34
27	30	32	22.50	70	8.53	26.51
28	35	53	26.25	65	12.91	40.14
29	25	53	26.25	65	22.02	64.38
30	35	39	18.75	65	15.09	46.94
31	25	39	18.75	65	11.74	34.33

a) Highest production capacity of the current work
b) Highest efficiency of the current work

Table S5. Results of the significance test for E and Pr of DPT

Efficiency, E(%)					Production capacity, Pr(100 g · mL^{-1})				
Term	Coef	SE Coef	T	P	Term	Coef	SE Coef	T	P
Constant	-1679.23	32.5252	-15.629	0.000	Constant	-496.993	32.9714	-15.073	0.000
	25.55	0.7368	34.682	0.000		6.325	0.3986	15.866	0.000
	18.48	0.5602	32.995	0.000		5.607	0.4155	13.493	0.000
	6.22	0.9404	6.610	0.000		2.828	0.7847	3.603	0.002
	24.30	0.7459	32.578	0.000		7.531	0.7631	9.869	0.000
	-0.22	0.0049	-44.607	0.000		-0.071	0.0052	-13.577	0.000
	-0.16	0.0054	-28.856	0.000		-0.047	0.0037	-12.783	0.000
	-0.14	0.0049	-29.119	0.000		-0.047	0.0052	-9.005	0.000
	-0.19	0.0058	-31.985	0.000		-0.050	0.0054	-9.149	0.000
	-0.04	0.0107	-3.550	0.004		0.017	0.0073	2.379	0.029
	-0.05	0.0087	-5.554	0.000		-0.050	0.0102	-4.893	0.000
	0.10	0.0077	12.837	0.000					
	-0.13	0.0107	-12.363	0.000					

Table S6. Analysis of variance for E and Pr of DPT

Source	Efficiency, E(%)					
	DF	Seq SS	Adj SS	Adj MS	F	P
Regression (model)	12	2869.32	2869.32	239.110	614.12	0.000
Linear	4	413.61	1413.96	353.491	907.90	0.000
Square	3	1846.02	1686.72	562.241	1444.04	0.000
Interaction	5	609.68	609.68	121.937	313.18	0.000
Residual Error	12	4.67	4.67	0.389		
Lack-of-Fit	6	4.09	4.09	0.681	6.96	0.016
Pure Error	6	0.59	0.59	0.098		
Total	24	2873.99				
Source	Production capacity, $Pr(100\ \mathrm{g}\cdot\mathrm{mL}^{-1})$					
	DF	Seq SS	Adj SS	Adj MS	F	P
Regression (model)	10	389.094	389.094	38.909	81.38	0.000
Linear	4	121.921	209.347	52.337	109.46	0.000
Square	3	203.540	196.677	65.559	137.12	0.000
Interaction	3	63.633	63.633	21.211	44.36	0.000
Residual Error	17	8.128	8.128	0.478		
Lack-of-Fit	11	8.068	8.068	0.733	72.89	0.000
Pure Error	6	0.060	0.010			
Total	27	397.222				

Table S7. The ANOVA of regression parameters for process parameters

Statistical analysis	Efficiency, E(%)	Production capacity
R-Sq	0.9984	0.9795
R-Sq(pred)	0.9871	0.9743
R-Sq(adj)	0.9967	0.9717
Difference between R-Sq(adj) and R-Sq(pred)	0.0096	0.0026
Lack of fit	0.0000	0.0160
PRESS	37.1940	30.4916

Table S8. Optimal set-up for E and Pr

Efficiency, E(%)	
Process parameters	Optimum value
x_1(mL)	30.0
x_2(°C)	46.0
x_3(min)	30.0
x_4(mL)	69.7290
Production capacity, $(100\ \mathrm{g}\cdot\mathrm{mL}^{-1})$	
Process parameters	Optimum value
x_1(mL)	30.0
x_2(°C)	47.6970
x_3(min)	30.0
x_4(mL)	64.6465

Table S9. Analysis of the confirmation of experiments for E and Pr

Responses	Predicted	Experimental	Error(%)
Efficiency, E(%)	23.0030	20.7700	9.71
Production capacity, $Pr(100\ \mathrm{g}\cdot\mathrm{mL}^{-1})$	64.9705	64.5800	0.60

Table S10. The amount of materials used in optimal method

Hexamine (g)	Ac_2O (mL)	AN-NA (mL)	Time of adding (min)	T (°C)
28.92	70	30	22	46

Table S11. The results of optimal method that was performed several times

No.	Efficiency, E(%)	Production capacity, $Pr(100\ \mathrm{g}\cdot\mathrm{mL}^{-1})$
1	61.99	19.94
2	62.58	20.13
3	62.47	20.09
4	62.88	20.22
5	62.05	19.95
6	62.21	20.01
7	62.34	20.05

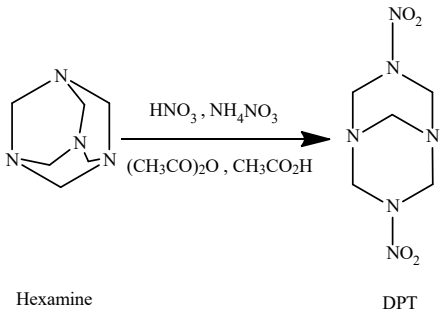

Figure S1. Nitration of hexamine.

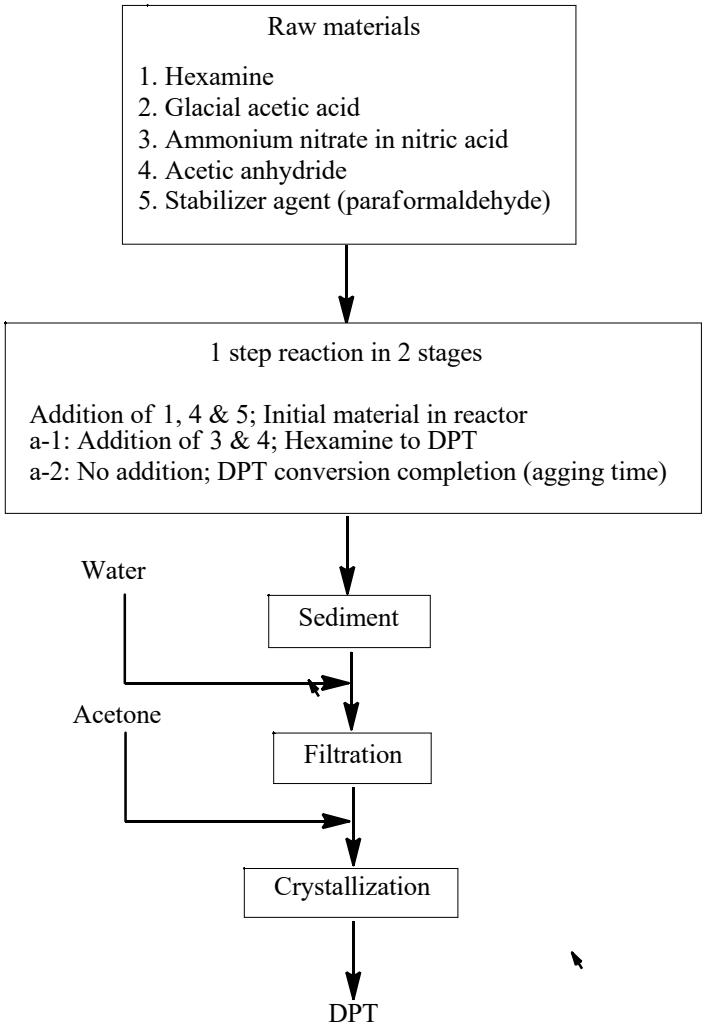

Figure S2. DPT synthesis setup.

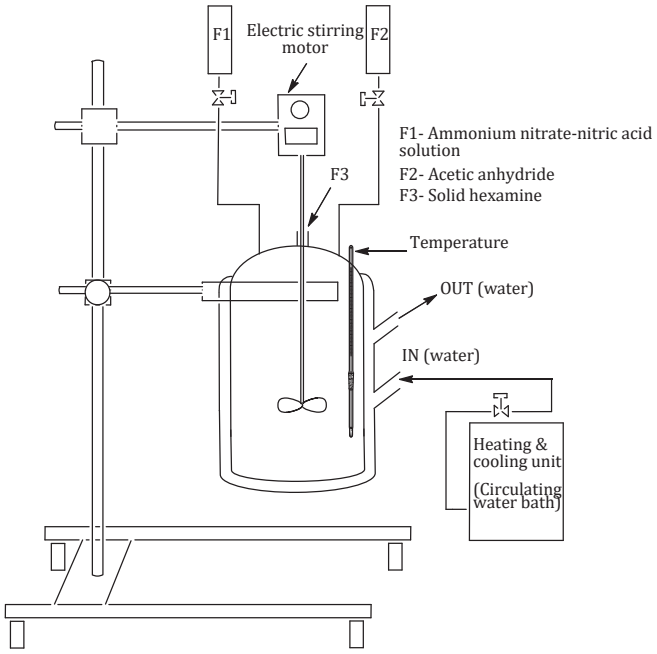

Figure S3. DPT synthesis scheme.

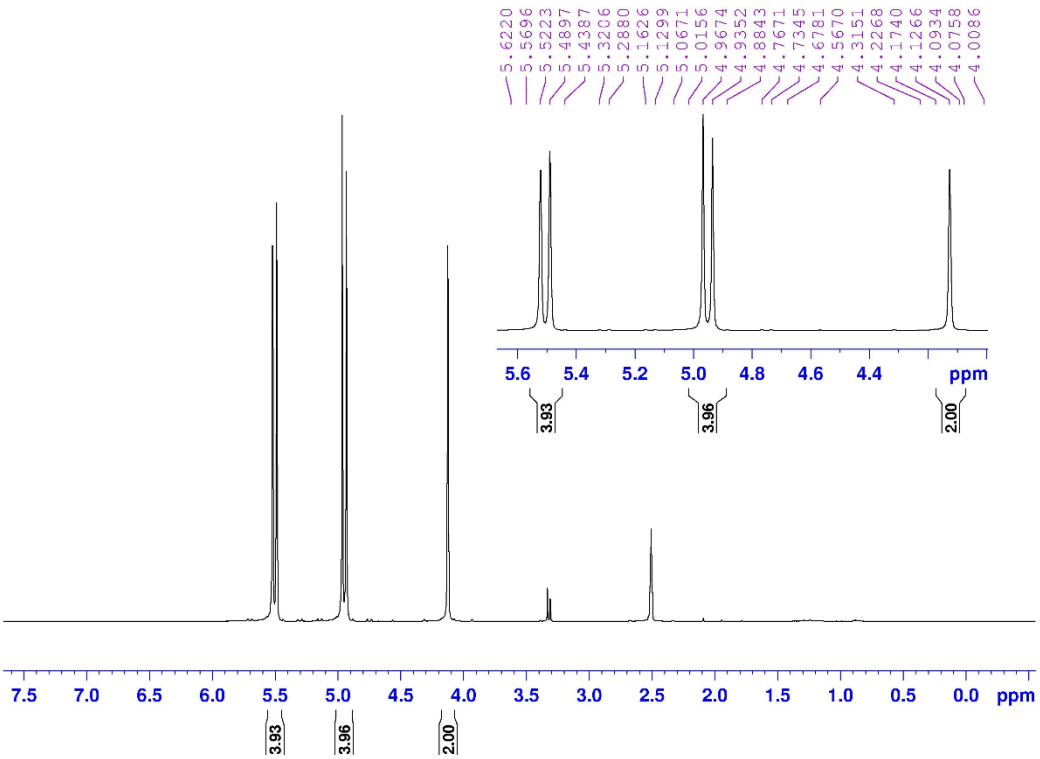

Figure S4. ^{1}H NMR spectrum of the synthesized DPT was scanned on 400 MHz.

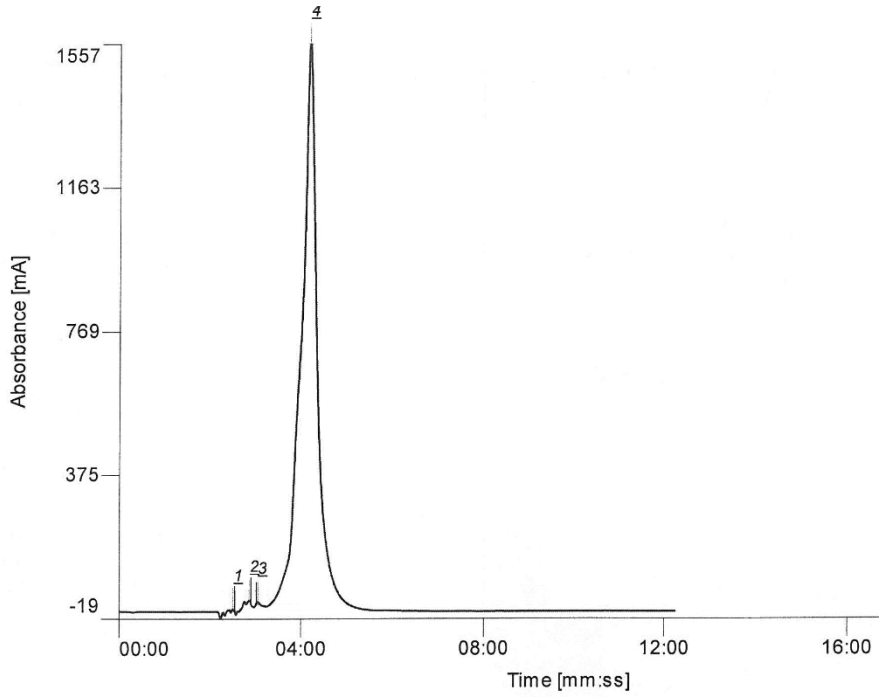

Figure S5. Chromatograph of synthesized DPT.

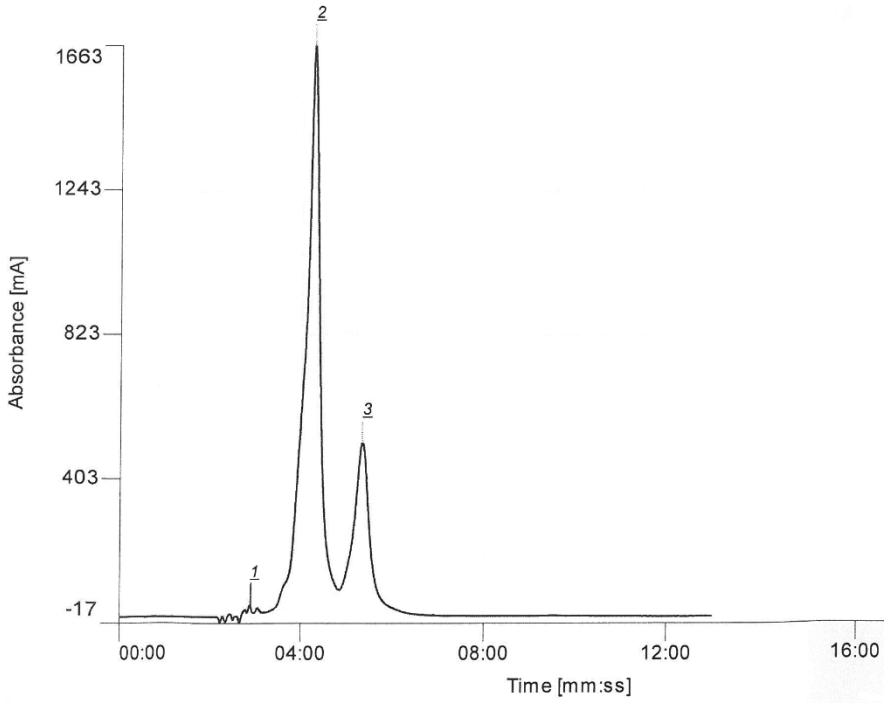

Figure S6. Chromatograph of the DPT containing HMX (0.055 %).

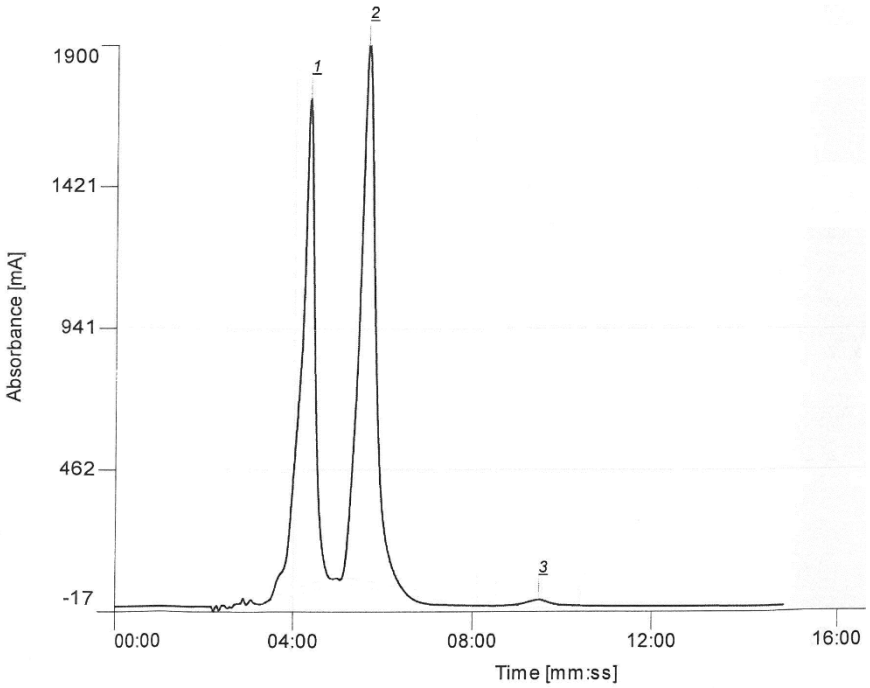

Figure S7. Chromatograph of the DPT containing α-HMX (0.096%).

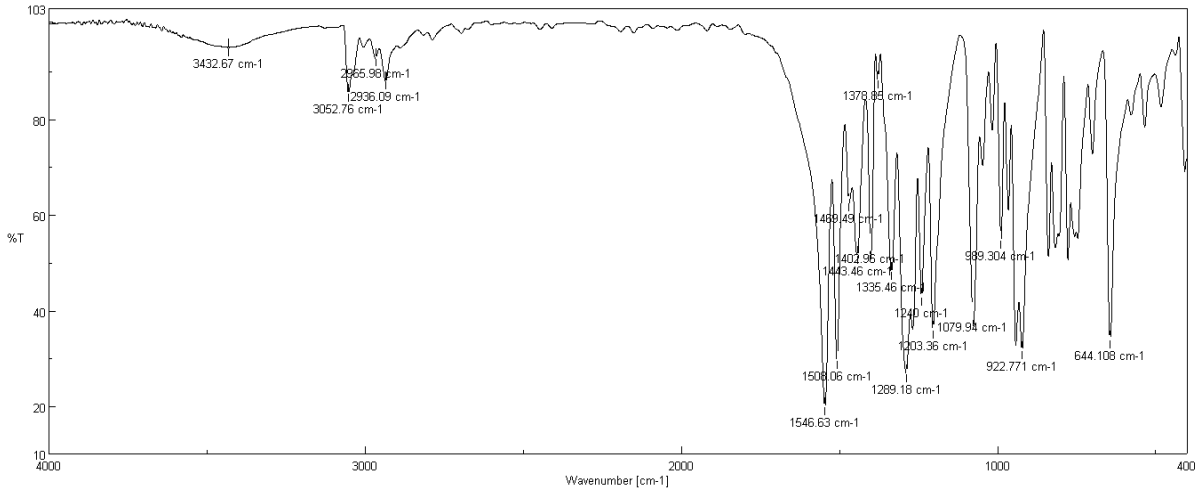

Figure S8. FT-IR spectrum for the synthesized DPT.

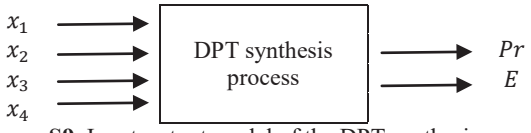

Figure S9. Input-output model of the DPT synthesis process

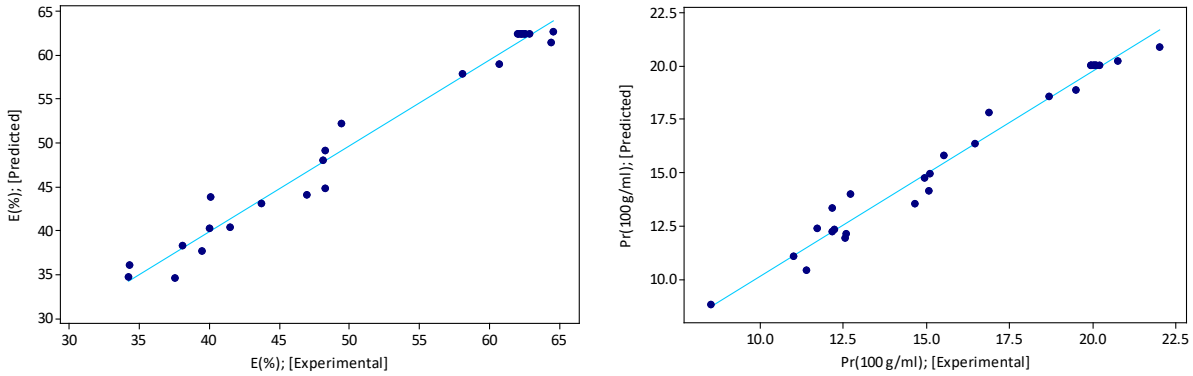

Figure S10. Comparison of the experimental results of Pr *and* E with those predicted via central composite design resulted equation (or Normal probability plot for Pr and E).

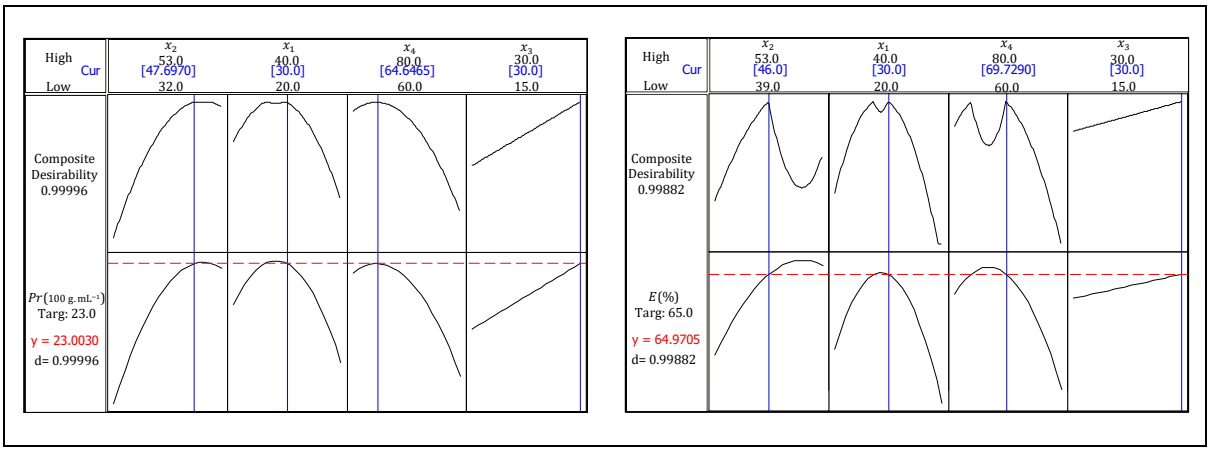

Figure S11. The optimized diagram of the parameters effective in E and Pr of DPT.

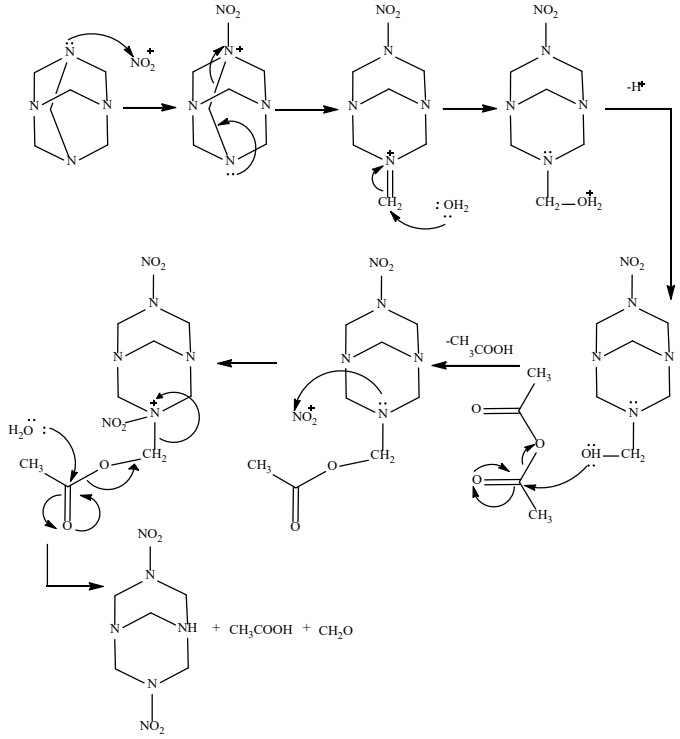

Figure S12. The suggested mechanism for the conversion of hexamine to DPT.

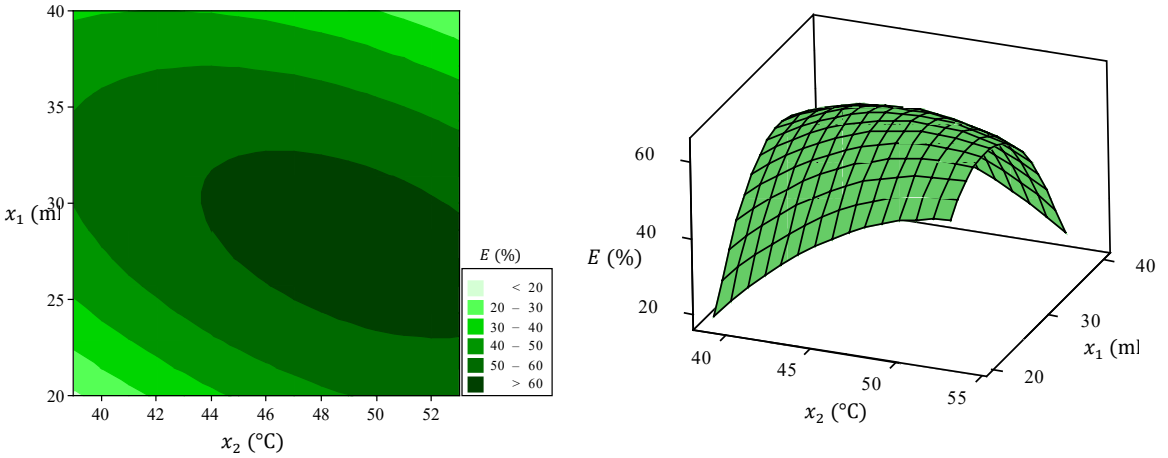

Figure S13. The contour and surface plots showing the effect of volume of AN–NA solution (x_1) on efficiency of DPT (hold values; x_3: 22.5 min and x_4: 70 mL).

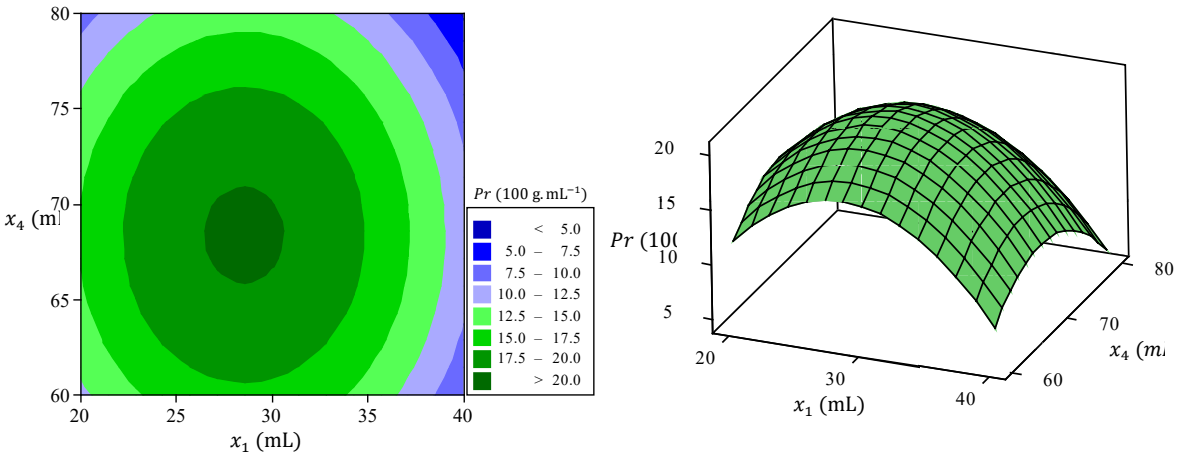

Figure S14. The contour and surface plots showing the effect of volume of AN–NA solution (x_1) on production capacity of DPT (hold values; x_2: 46 °C and x_3: 22.5 min).

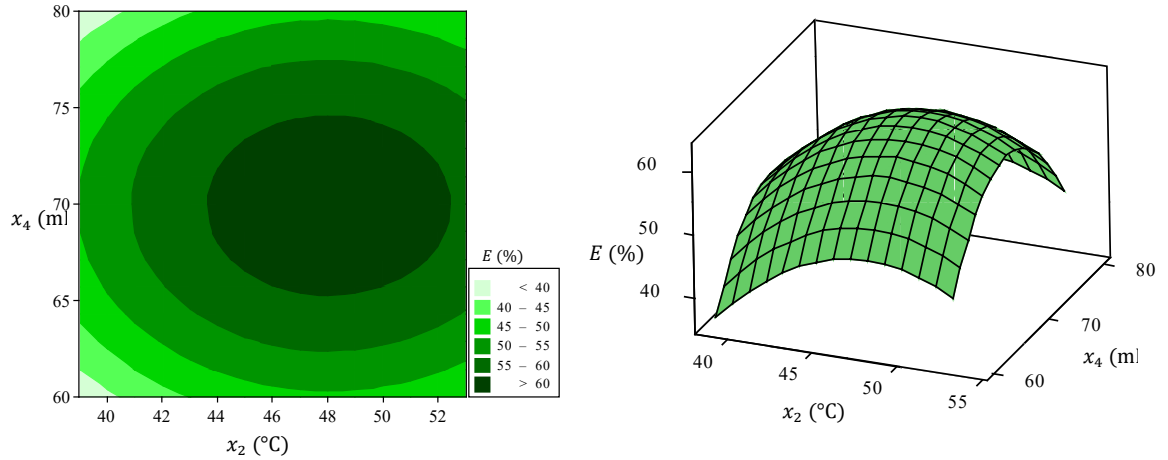

Figure S15. The contour and surface plots showing the effect of nitration temperature (x_2) on efficiency of DPT (hold values; x_1: 30 mL and x_3: 22.5 min).

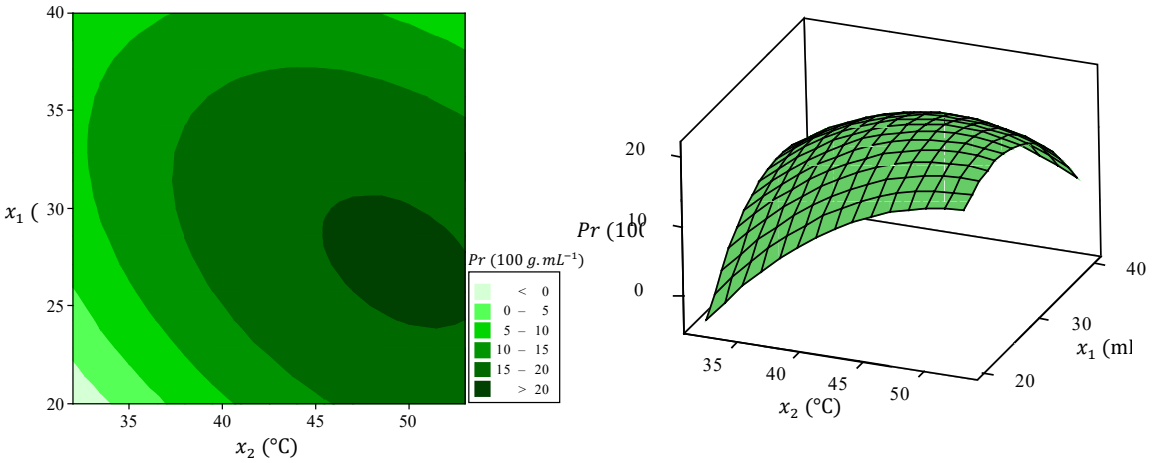

Figure S16. The contour and surface plots showing the effect of nitration temperature (x_2) on production capacity of DPT (hold values; x_3: 22.5 min and x_4: 70 mL).

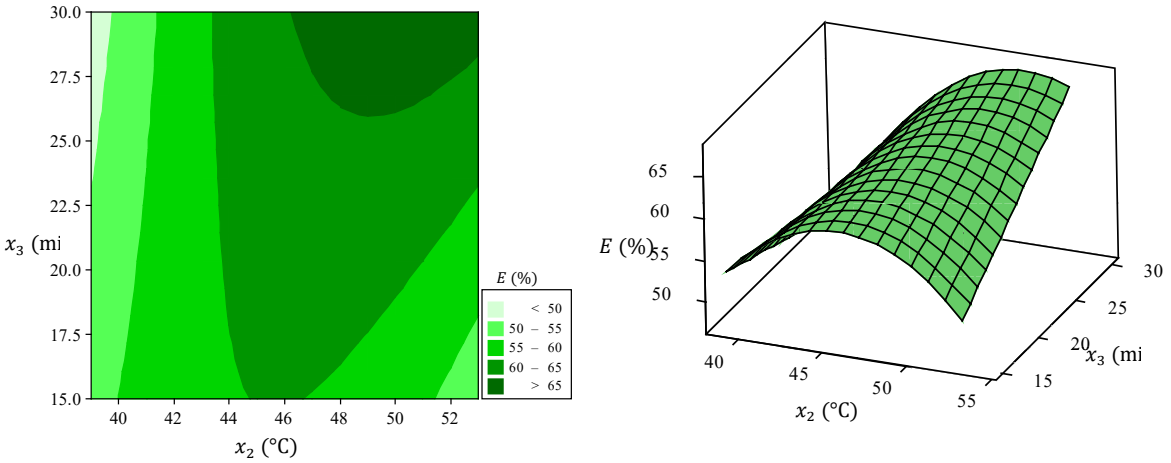

Figure S17. The contour and surface plots showing the effect of time of adding to the reactor (x_3) on efficiency of DPT (hold values; x_1: 30 mL and x_4: 70 mL).

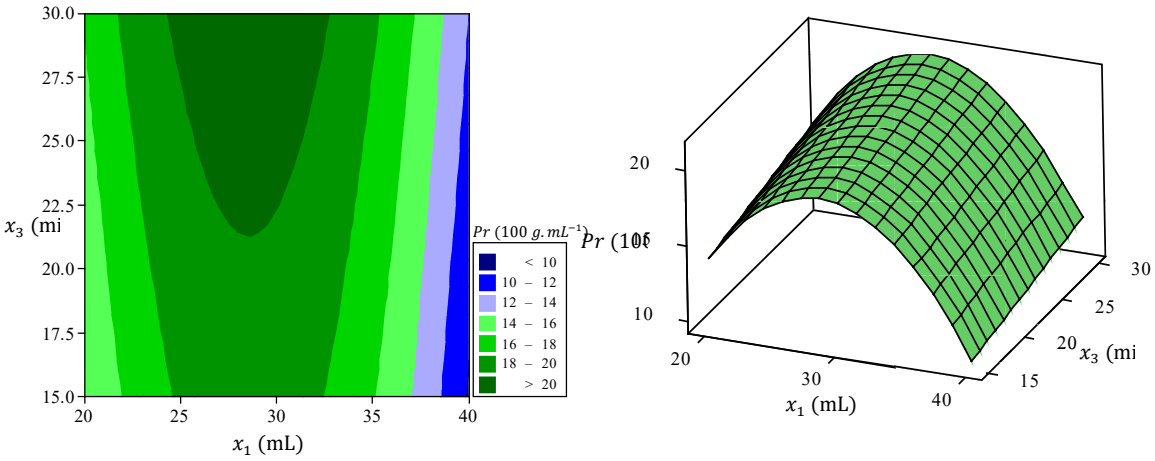

Figure S18. The contour and surface plots showing the effect of time of adding to the reactor (x_3) on production capacity of DPT (hold values; x_2: 46 °C and x_4: 70 ml).

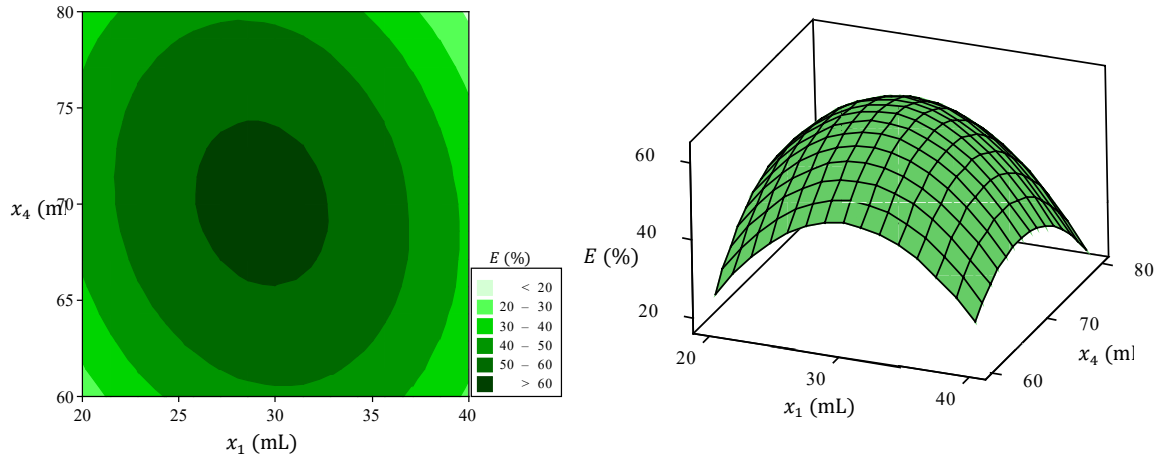

Figure S19. The contour and surface plots showing the effect of volume of acetic anhydride (x_4) on efficiency of DPT (hold values; x_2: 46 °C and x_3: 22.5 min).

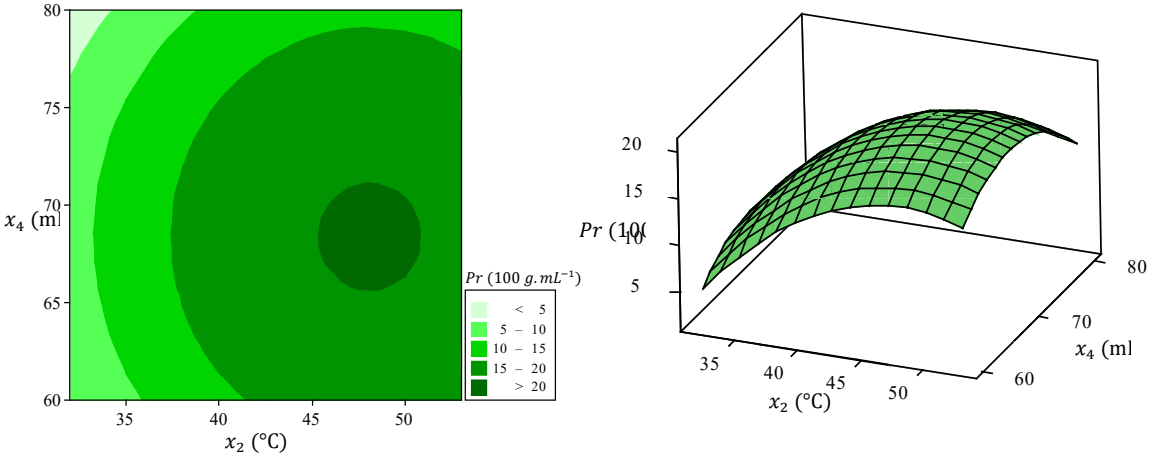

Figure S20. The contour and surface plots showing the effect of volume of acetic anhydride (x_4) on production capacity of DPT (hold values;. x_1: 30 mL and x_3: 22.5 min).