Optimization of a Chemical Looping Process by Optimal DOE and Statistical Modeling

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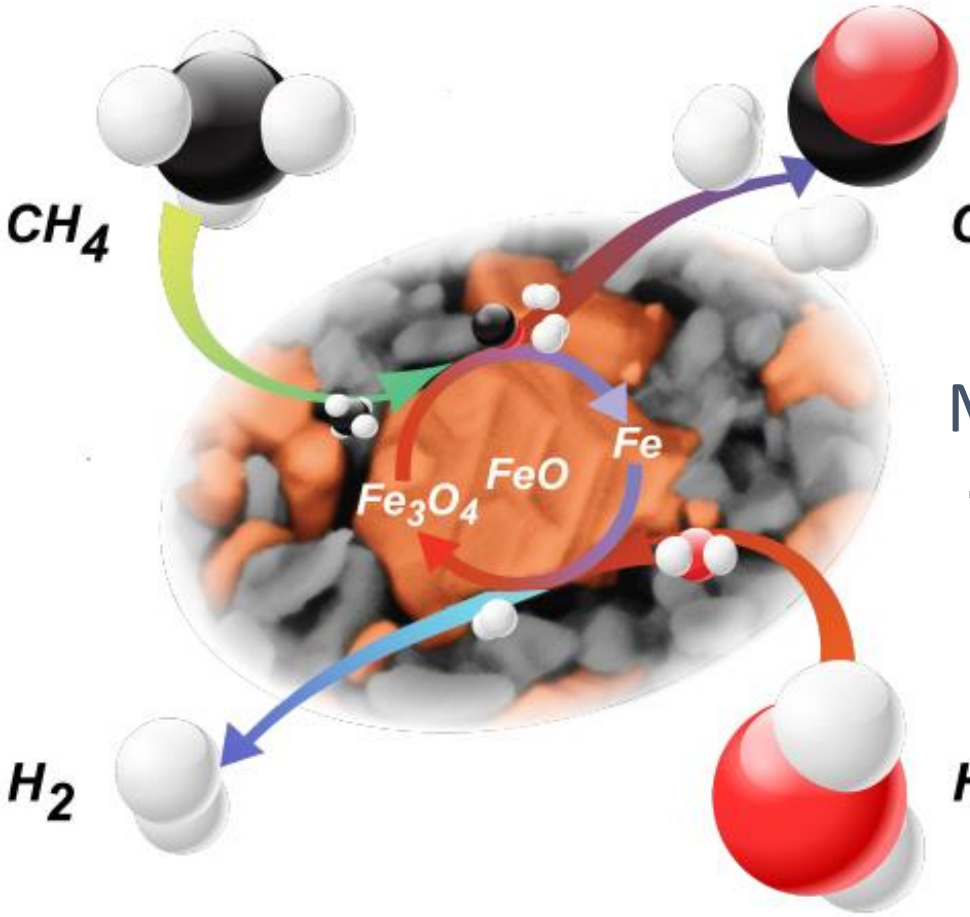
Chemical looping

Partial oxidation hydrocarbons in fluidized bed reactor → Synthesis Gas

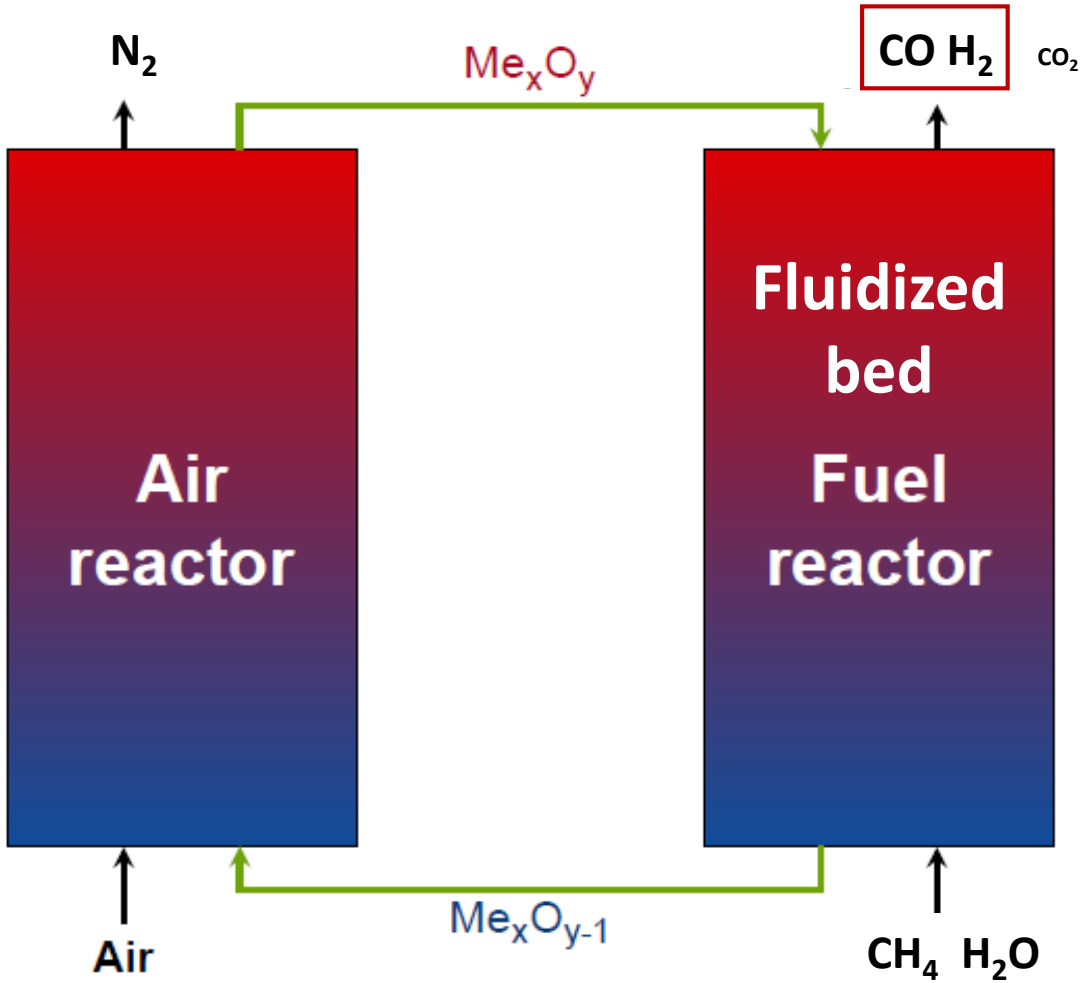


$CO + 2\,H_2$ → **Chemicals**

Metal Oxide "Me_xO_y" solid **Oxygen Carrier** (OC)
→ selective oxygen transfer

Oxidizing agent → air & **CO_2** also possible

Chemical Looping Steam Reforming



No dilution produced gases by air N_2

Lower gas separation costs during postprocessing

Easier separation of CO_2 by-product

Goal – Model – DOE

Model pilot plant fluidized bed reactor process so "Design Space" optimal chemical looping performance can be specified

Goal – Model – DOE

MODEL $Y_i = f(X_i)$

Response variables Y_i

- The time until the OC was completely reduced, t_{red} **Minimise**

- The average conversion of methane, X_{av} **Maximise**
- The conversion of methane at the point where maximum CO_2-production occurs; $X_{CO_2,max}$
- The absolute Yield of H_2 per hour during the oxygen carrier reduction, $\dot{Y}_{H_2,abs}$

Goal – Model – DOE

Input variables X_i

$T_{reactor}$	m_{OC}	c_{CH_4}	$\dot{V}_{total}$	$T_{sintering}$	Size	Plate
x1	x2	x3	x4	x5	x6	x7
[°C]	[g]	[V%]	[sccm]	[°C]		

2-level categorical

Reactor conditions

Reactor temperature		CH_4 concentration	
	$T_{reactor}$ x1 [°C]		c_{CH_4} x3 [V%]
900°C		30%	
870°C		20%	
930°C		40%	

Particle properties

Sintering temperature		Particle size	Size x6
	$T_{sintering}$ x5 [°C]		
1175°C		106-150 µm	
1140°C		150-212 µm	
1210°C			

Fluidisation properties

$\dot{V}_{total}$ x4 [sccm]

Volume flow		Bed mass		Porous plate	Plate x7
		m_{OC} x2 [g]			
110 sccm		2 g		A = 100-160 µm	
80 sccm		1.5 g		B = 40-100 µm	
140 sccm		2.5 g			

7 controllable process parameters

max 4 runs/day

+ blocking factor "Day"

Goal – Model – DOE

$$Y_{ij} = \beta_0 + \sum_{k=1} \beta_k x_{kij} + \sum_{k=1} \sum_{l=k+1} \beta_{kl} x_{kij} x_{lij} + \sum_{i=1} \beta_{kk} x_{kij}^2 + \gamma_i + \varepsilon_{ij}$$

intercept

residual error
response run-to-run
variation

Fixed main, interaction & quadratic effects

MIXED MODEL

RESPONSE SURFACE DESIGN

MODEL WITH FIXED EFFECTS & BLOCKS

Random block effect "Day"
models the day-to-day differences between the responses

(*) Ref. OPTIMAL DESIGN OF EXPERIMENTS A Case Study Approach
PETER GOOS & BRADLEY JONES

Goal – Model – DOE

Sequential DOE Strategy

Non Orthogonal DOE
Blocked DSD or Custom DOE

1. D-Optimal Screening DOE

Estimate pure main effects, quadratic parameters

2^{nd} order interactions → limited alias/correlation

(!) # experiments < 40 9 – 10 days & max 4 runs/day

No option→ fractional 2^{7-3} resolution IV + center/axial runs

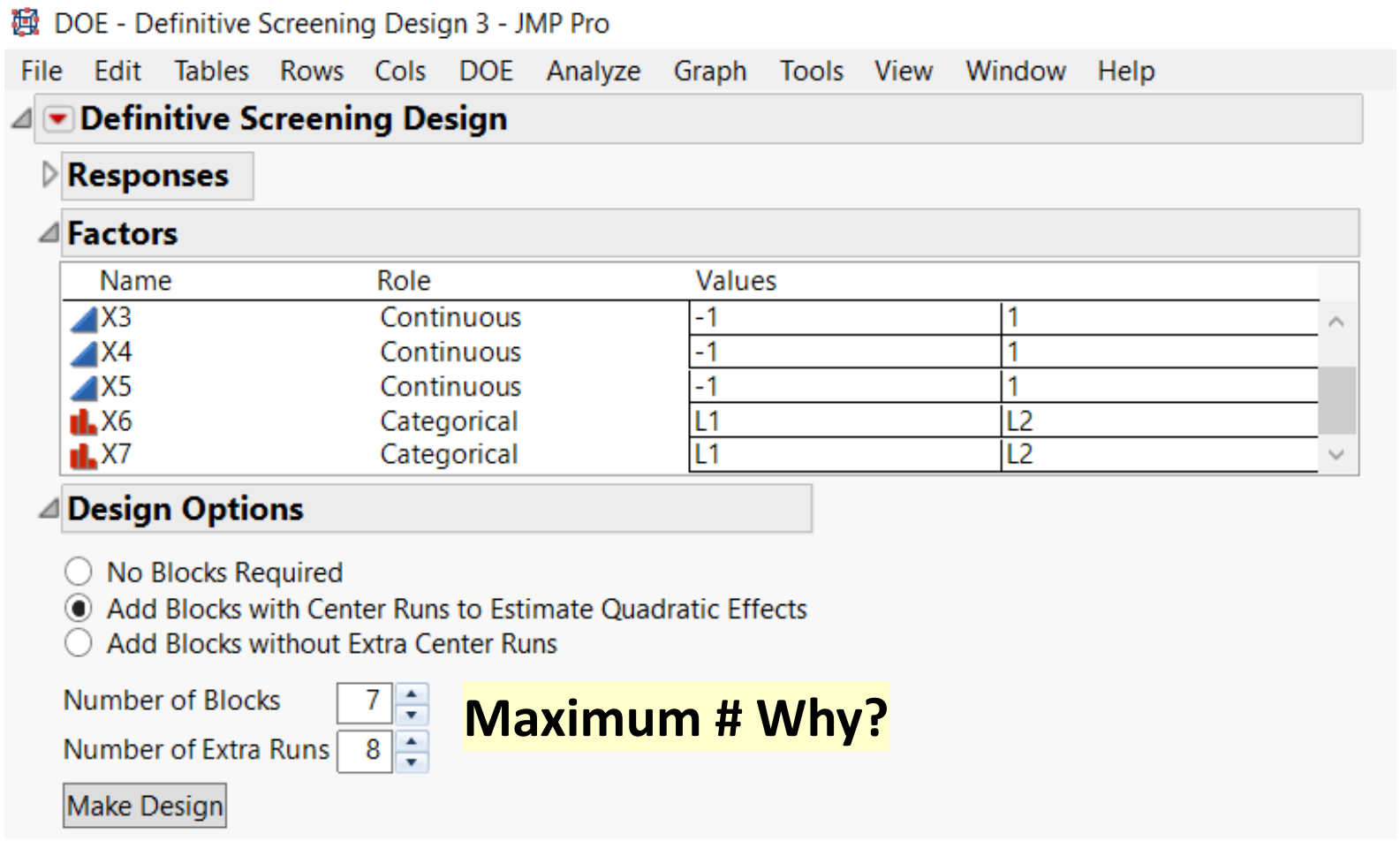
2. Response Surface Model (RSM)

Full quadratic polynomial model → Response optimization

Augment Screening DOE with limited extra runs

Goal – Model – DOE

Blocked Definitive Screening Design (DSD)

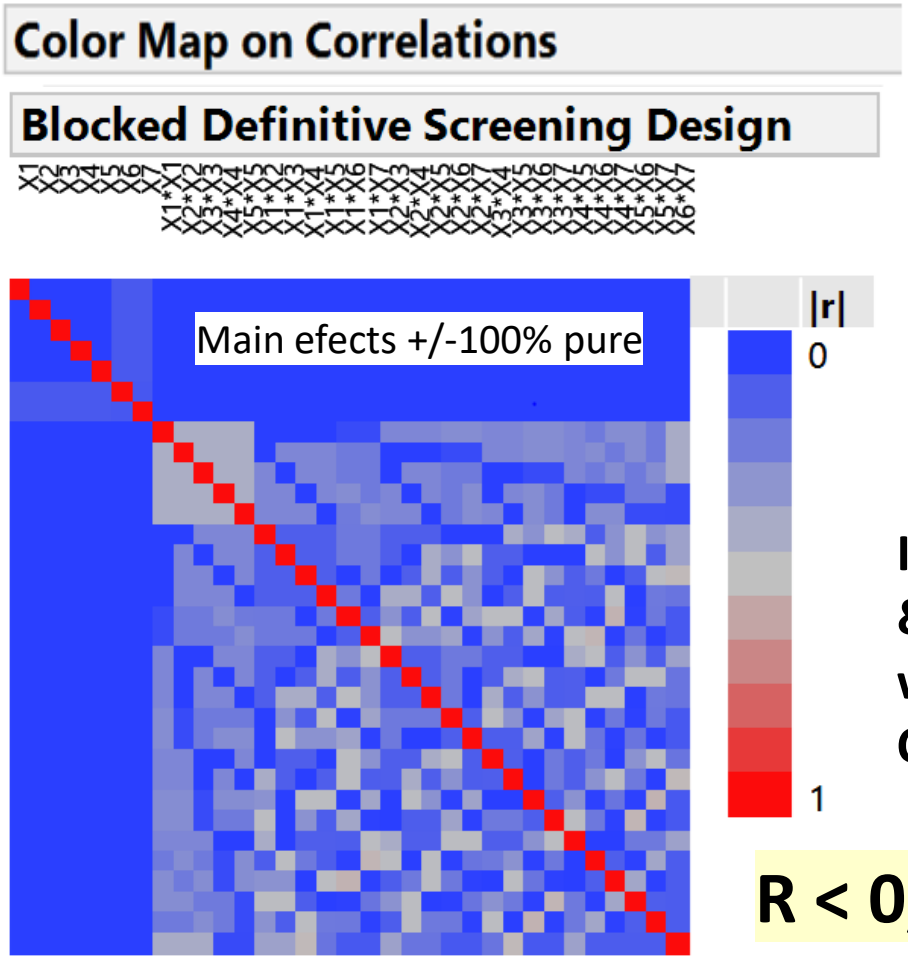


Maximum # Why?

Goal – Model – DOE

Blocked Definitive Screening Design (DSD)

	Block	X1	X2	X3	X4	X5	X6	X7	Y
1	1	1	1	-1	-1	-1	L2	L1	•
2	1	0	-1	-1	-1	-1	L1	L1	•
3	1	0	1	1	1	1	L2	L2	•
4	1	-1	-1	1	1	1	L1	L2	•
5	2	-1	0	-1	1	-1	L1	L1	•
6	2	1	1	1	-1	-1	L1	L2	•
7	2	1	0	1	-1	1	L2	L2	•
8	2	-1	-1	-1	1	1	L2	L1	•
9	3	1	1	1	1	-1	L1	L1	•
10	3	1	-1	0	1	-1	L2	L2	•
11	3	-1	-1	-1	-1	1	L2	L2	•
12	3	-1	1	0	-1	1	L1	L1	•
13	4	1	1	-1	0	1	L1	L2	•
14	4	-1	1	-1	-1	-1	L2	L2	•
15	4	-1	-1	1	0	-1	L2	L1	•
16	4	1	-1	1	1	1	L1	L1	•
17	5	-1	-1	1	-1	-1	L1	L2	•
18	5	1	-1	1	-1	0	L2	L1	•
19	5	-1	1	-1	1	0	L1	L2	•
20	5	1	1	-1	1	1	L2	L1	•
21	6	0	0	0	0	0	L1	L1	•
22	6	1	-1	-1	1	-1	L2	L2	•
23	6	-1	1	1	-1	1	L1	L1	•
24	6	0	0	0	0	0	L2	L2	•
25	7	-1	1	1	1	-1	L2	L1	•
26	7	1	-1	-1	-1	1	L1	L2	•

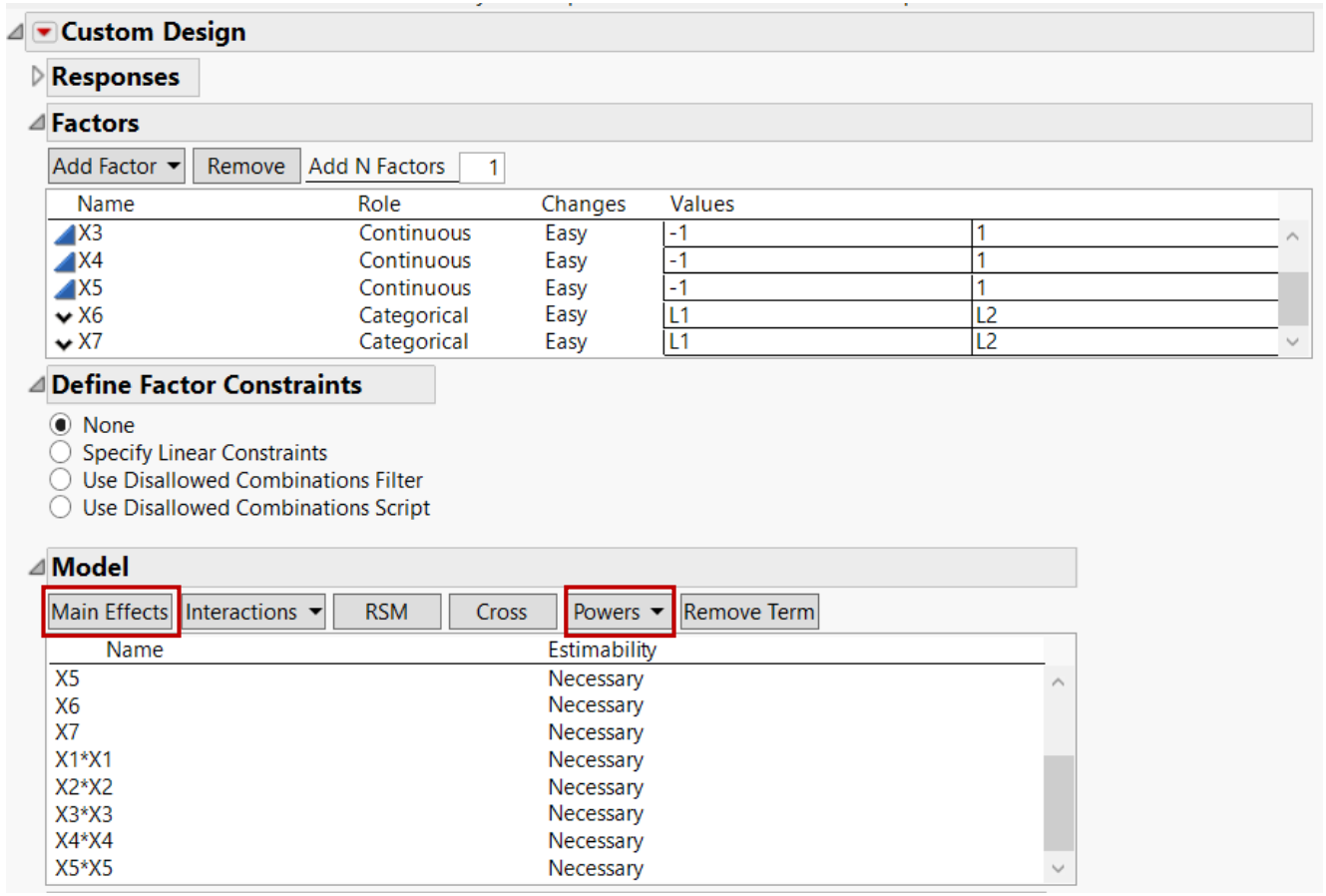


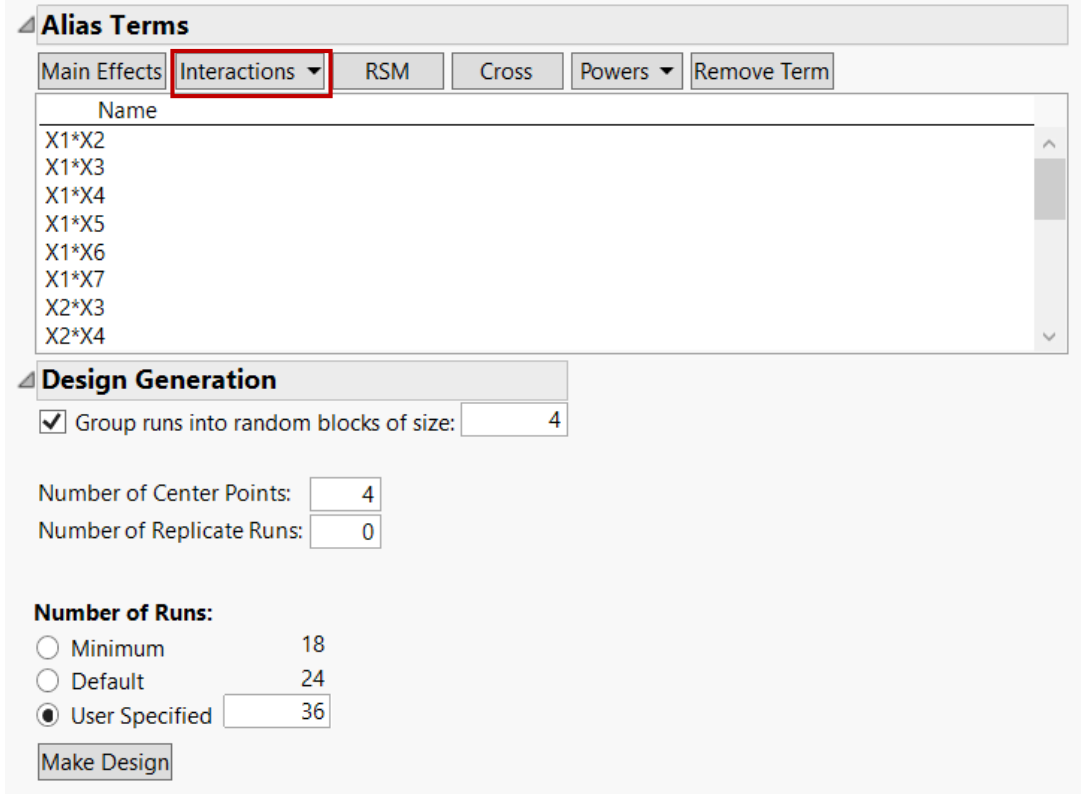
Increase testing power & prediction variance with more runs → Custom DOE

R < 0,6 → acceptable

Goal – Model – DOE

Custom Design

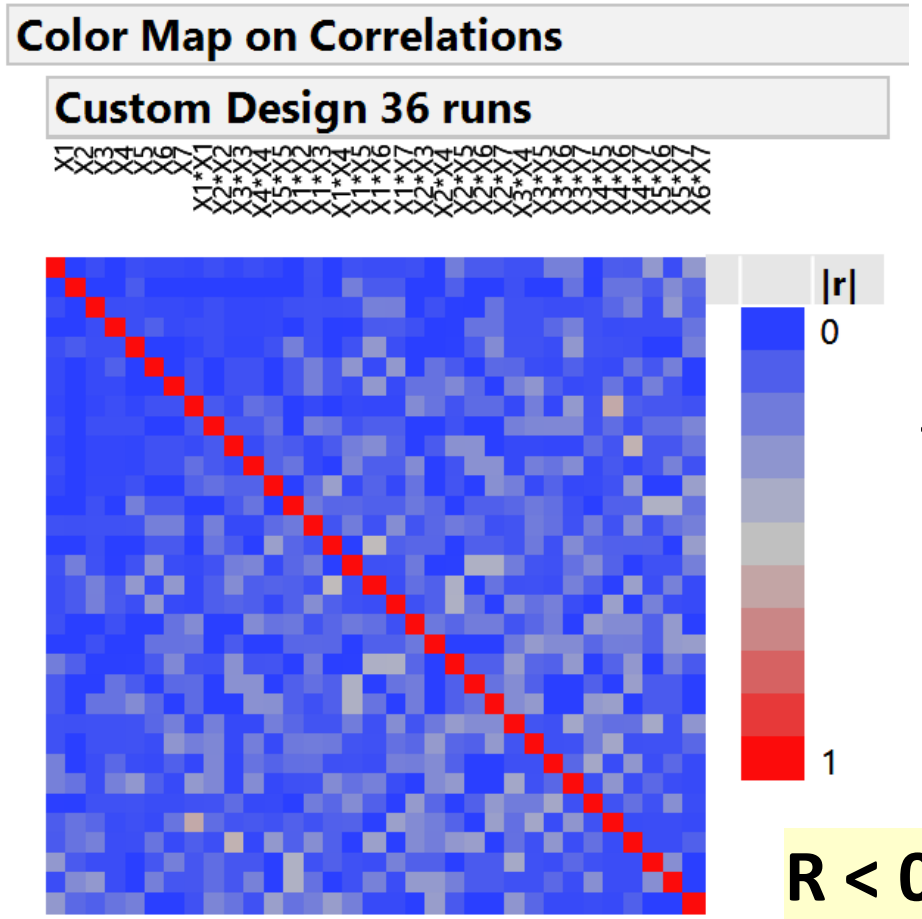




Goal – Model – DOE

Custom Design

	Random Block	X1	X2	X3	X4	X5	X6	X7	Y
1	1	0	-1	0	-1	1	L2	L1	•
2	1	1	-1	-1	-1	0	L1	L2	•
3	1	1	0	-1	1	0	L2	L1	•
4	1	-1	1	1	0	-1	L1	L2	•
5	2	1	1	0	-1	-1	L2	L1	•
6	2	0	-1	-1	1	1	L1	L1	•
7	2	0	0	1	1	1	L1	L2	•
8	2	-1	-1	-1	0	0	L2	L2	•
9	3	-1	1	1	1	1	L2	L1	•
10	3	0	0	0	0	0	L2	L2	•
11	3	1	-1	-1	-1	-1	L1	L2	•
12	3	0	0	0	0	0	L1	L1	•
13	4	1	0	1	-1	1	L1	L1	•
14	4	-1	1	0	1	-1	L1	L2	•
15	4	0	1	-1	0	-1	L2	L1	•
16	4	1	-1	0	1	0	L2	L2	•
17	5	1	0	0	1	-1	L2	L2	•
18	5	-1	-1	1	0	0	L1	L1	•
19	5	0	0	0	0	0	L1	L1	•
20	5	0	1	-1	-1	1	L2	L2	•
21	6	0	0	0	0	0	L1	L2	•
22	6	1	1	1	1	0	L2	L1	•
23	6	-1	0	-1	-1	-1	L1	L1	•
24	6	-1	-1	0	1	1	L2	L2	•
25	7	-1	0	-1	1	-1	L2	L1	•
26	7	-1	-1	0	-1	1	L1	L1	•
27	7	0	1	1	-1	0	L2	L2	•
28	7	1	1	-1	0	1	L1	L2	•
29	8	0	-1	1	1	-1	L1	L2	•
30	8	-1	1	0	-1	0	L1	L1	•
31	8	-1	0	-1	0	1	L2	L2	•
32	8	1	-1	1	0	1	L2	L1	•
33	9	-1	0	1	-1	0	L2	L2	•
34	9	0	1	-1	1	0	L1	L1	•
35	9	0	-1	1	0	-1	L2	L1	•
36	9	1	1	0	0	1	L1	L2	•



+/- pure main effects

Compared to DSD → quadratic effects less correlated

R < 0,6 → acceptable

Goal – Model – DOE

Compare designs Custom DOE vs. Blocked DSD

DOE Diagnostics

Design Evaluation

Power Analysis

Significance Level 0,05

Anticipated RMSE 1

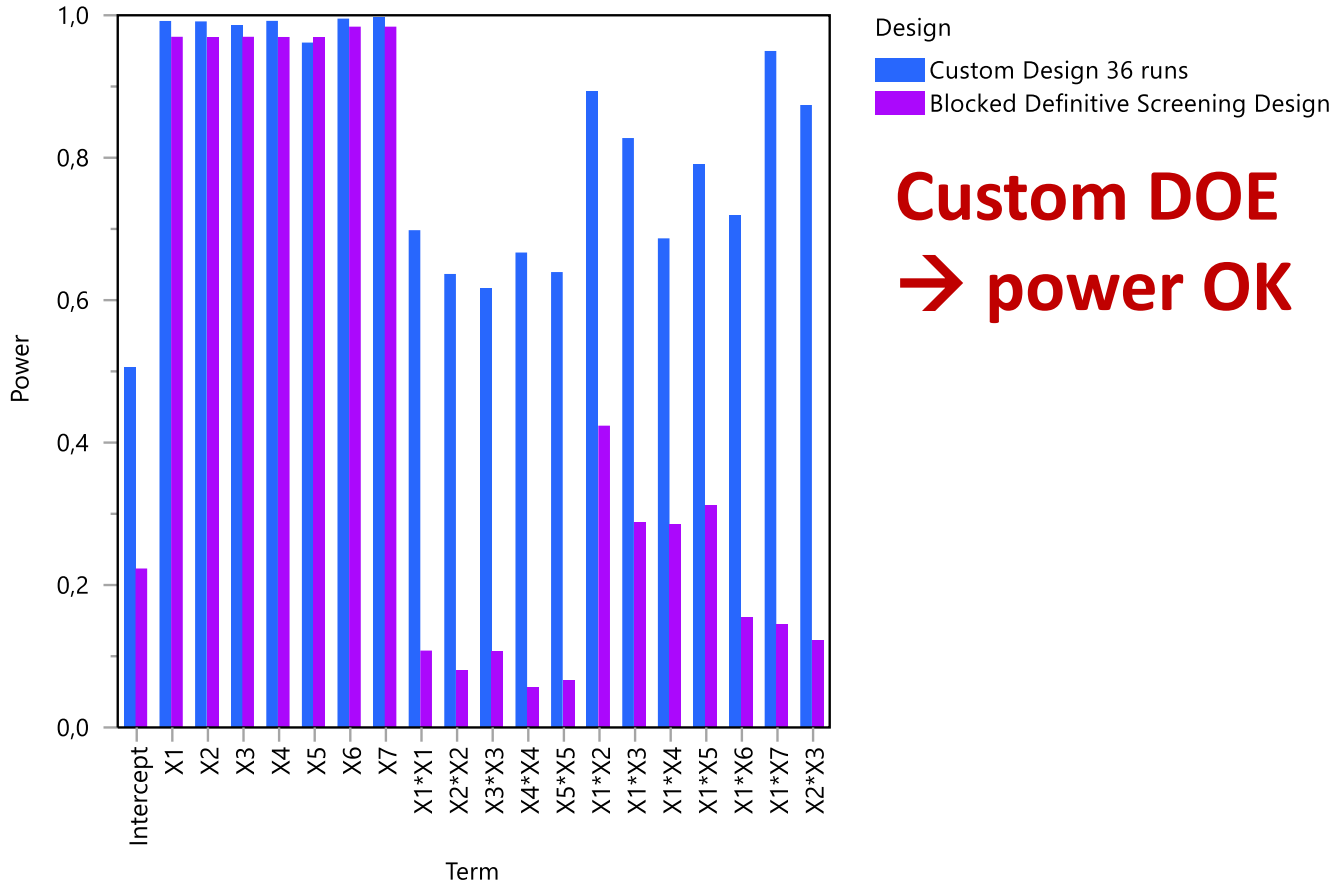
Poor power quadratic & interaction effects

Term	Anticipated Coefficient	Custom Design 36 runs Power	Blocked Definitive Screening Design Power
Intercept	1	0,507	0,223
X1	1	0,992	0,970
X2	1	0,991	0,970
X3	1	0,986	0,970
X4	1	0,992	0,970
X5	1	0,962	0,970
X6	1	0,995	0,984
X7	1	0,998	0,984
X1*X1	1	0,698	0,108
X2*X2	1	0,637	0,081
X3*X3	1	0,617	0,107
X4*X4	1	0,667	0,057
X5*X5	1	0,639	0,067
X1*X2	1	0,894	0,424
X1*X3	1	0,828	0,288
X1*X4	1	0,687	0,286
X1*X5	1	0,791	0,313
X1*X6	1	0,720	0,156
X1*X7	1	0,950	0,145
X2*X3	1	0,874	0,123

Apply Changes to Anticipated Coefficients

Good 0,80 0,60 0,40 0,20 Bad

Power Plot

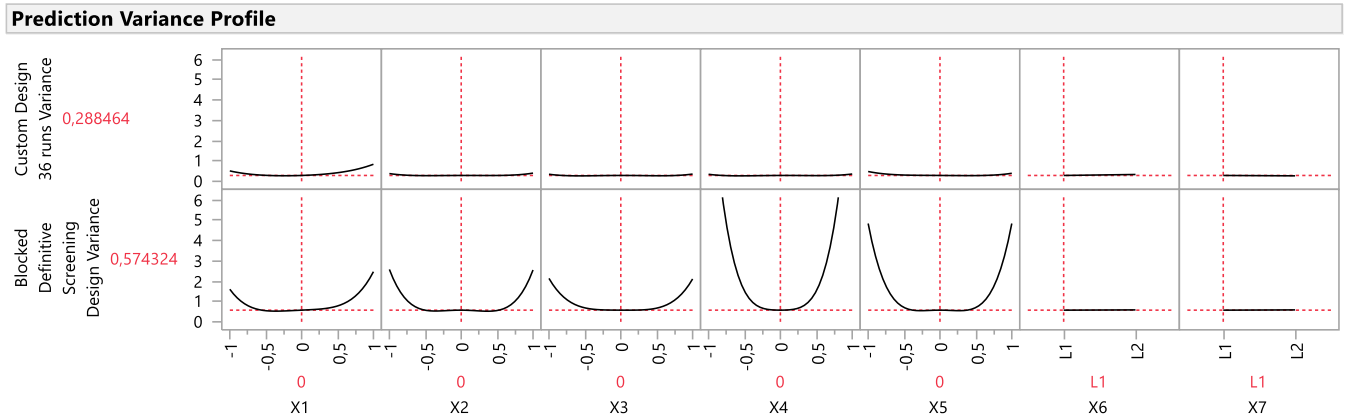


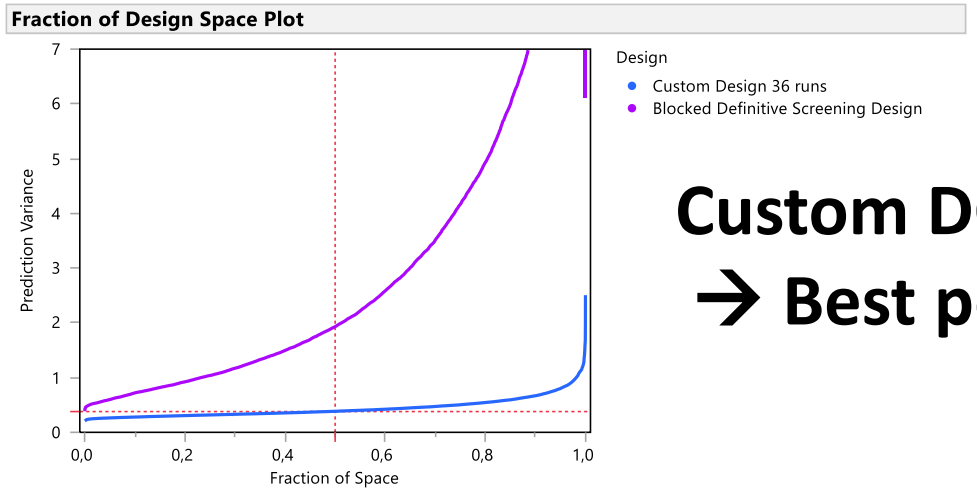
Custom DOE → power OK

Goal – Model – DOE

Compare designs Custom DOE vs. Blocked DSD

DOE Diagnostics





Custom DOE

→ Best performance

Relative Estimation Efficiency

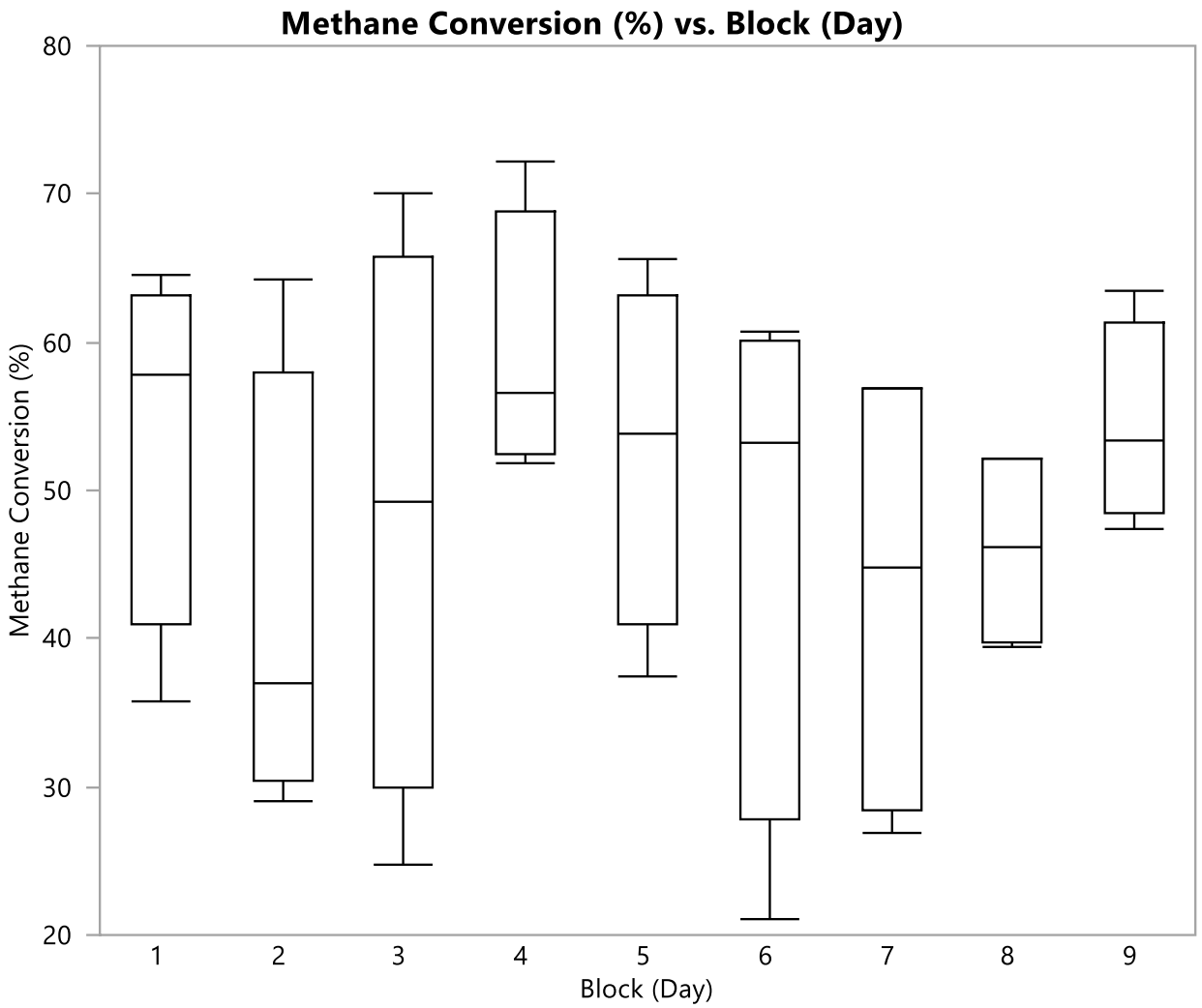
Term	Efficiency of Custom Design 36 runs Relative to Blocked Definitive Screening Design
Intercept	1,487
X1	1,001
X2	0,995
X3	0,952
X4	1,003
X5	0,855
X6	0,974
X7	1,020
X1*X1	3,198
X2*X2	4,048
X3*X3	2,943
X4*X4	8,741
X5*X5	5,504
X1*X2	1,627
X1*X3	1,867
X1*X4	1,578
X1*X5	1,692
X1*X6	2,441
X1*X7	3,657
X2*X3	3,582

Good — Bad

1,50 1,25 0,80 0,67

Analysis Custom DOE Results

Graph Builder



Predictor Screening

	Methane Conversion (%)			
Predictor	**Contribution**	**Portion**		**Rank**
Block (Day)	426,230	0,2799		1
T sintering	402,306	0,2642		2
Treactor	388,810	0,2553		3
V	87,082	0,0572		4
m	78,303	0,0514		5
Plate	49,987	0,0328		6
c	47,448	0,0312		7
Size	42,507	0,0279		8

Significant random day-to-day variation!

Analysis Custom DOE Results

Random block effect "Day" → MIXED MODEL

→ Restricted Maximum Likelihood "REML" estimation"

Remove random day-to-day time variation from run-to-run variation

REML no forward stepwise regression!

Hard to estimate 33 RSM effects with 36 runs

Analysis strategy

1. **Stepwise forward Regression → RSM "Day" = block fixed effect**
   Screen out significant effects

2. **REML → Final RSM "Day" = random block effect**

Analysis Custom DOE Results

Response Methane Conversion (%)

Effect Summary

Source	LogWorth	PValue
Size*Plate	.	.
T sintering*Plate	.	.
V*Plate	.	.
c*Plate	.	.
m*Plate	.	.
Treactor*Plate	.	.
T sintering*Size	.	.
V*Size	.	.
c*Size	.	.
m*Size	.	.
Treactor*Size	.	.
T sintering*T sintering	.	.
V*T sintering	.	.
c*T sintering	.	.
m*T sintering	.	.
Treactor*T sintering	.	.
V*V	.	.
c*V	.	.
m*V	.	.
Treactor*V	.	.
c*c	.	.
m*c	.	.
Treactor*c	.	.
m*m	.	.
Treactor*m	.	.
Treactor*Treactor	.	.
Plate	.	.
Size	.	.
T sintering	.	.
V	.	.
c	.	.
m	.	.
Treactor	.	.

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Wald p-Value	Pct of Total
Block (Day)	0	0	1,5909903	-3,118284	3,1182836	1,0000	0,000
Residual		1,125	0	.	.		100,000
Total		1,125	0	.	.		100,000

-2 LogLikelihood = 288,83565421

Note: Total is the sum of the positive variance components.

Total including negative estimates = 1,125

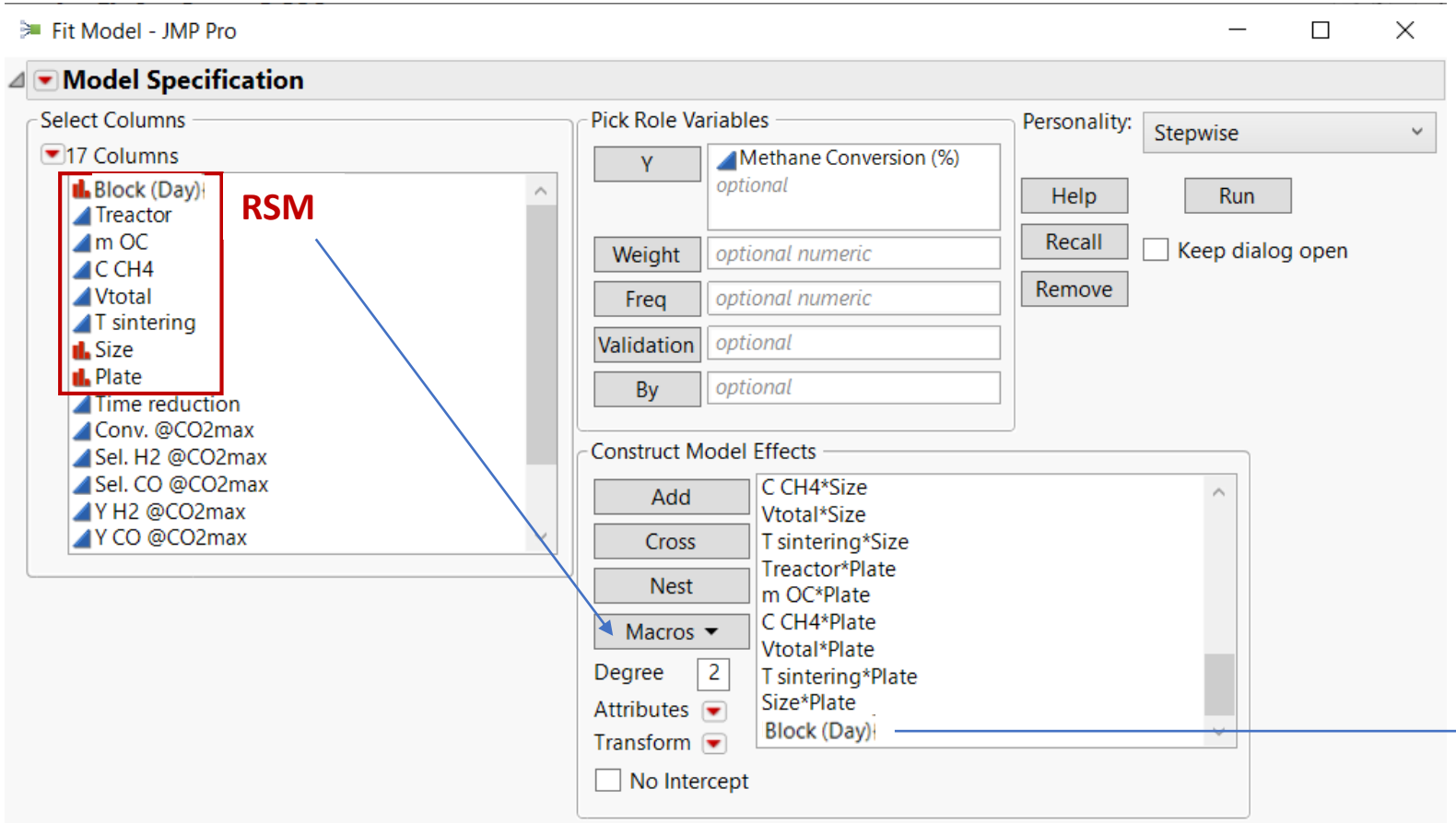
REML → Backward regression 33 effects?

Stepwise Forward REML regression not possible?

Analysis Custom DOE Results

Analysis strategy

1. Stepwise Regression

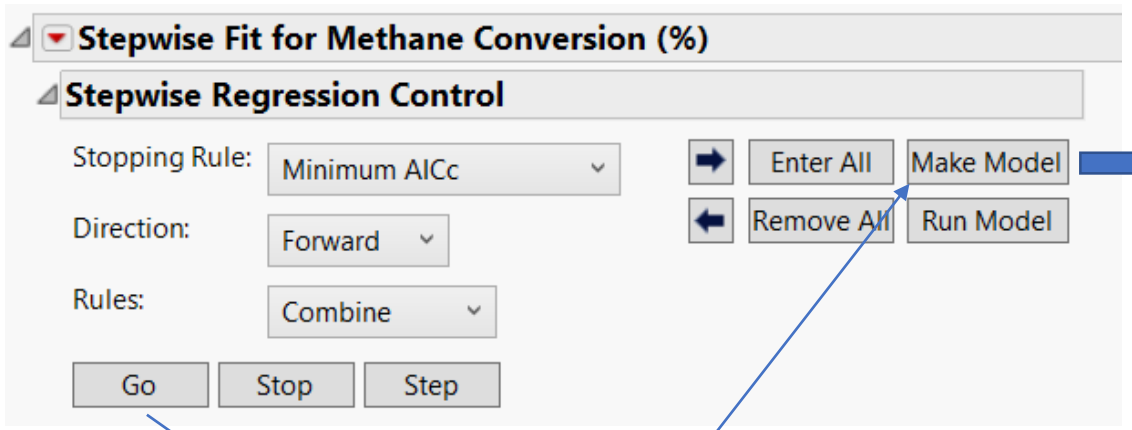


Block (Day) = fixed effect

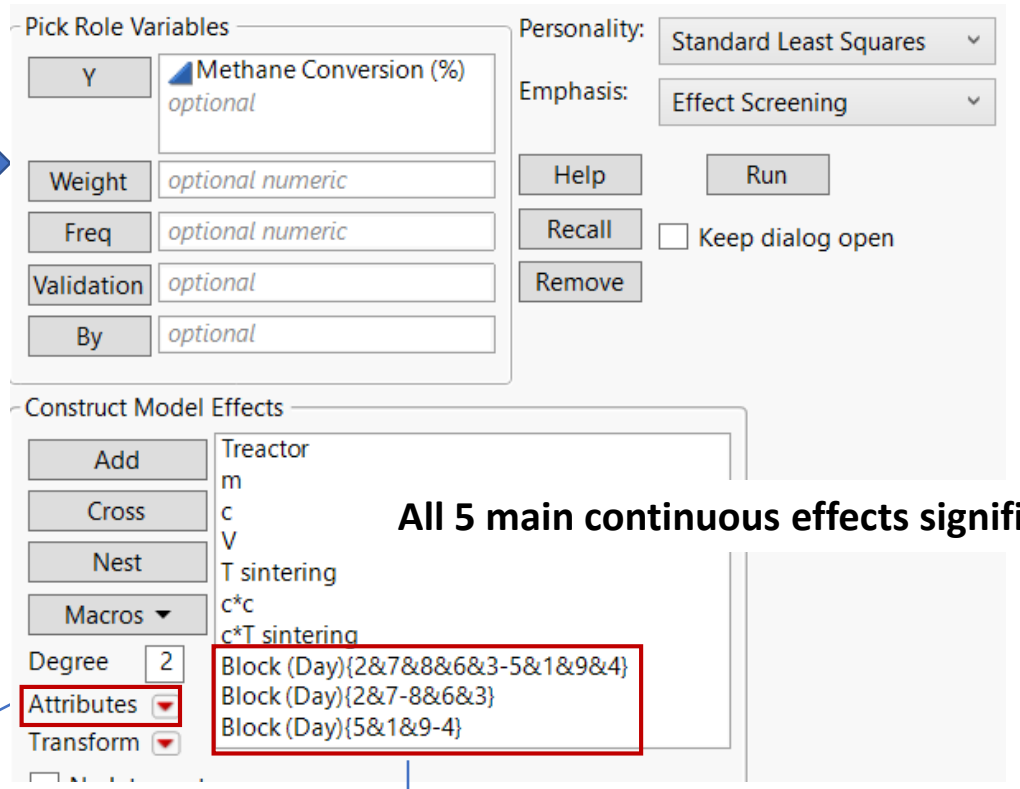
Analysis Custom DOE Results

Analysis strategy

1. Stepwise Regression



Same results with "All Possible Models"



Significant effects

All 5 main continuous effects significant

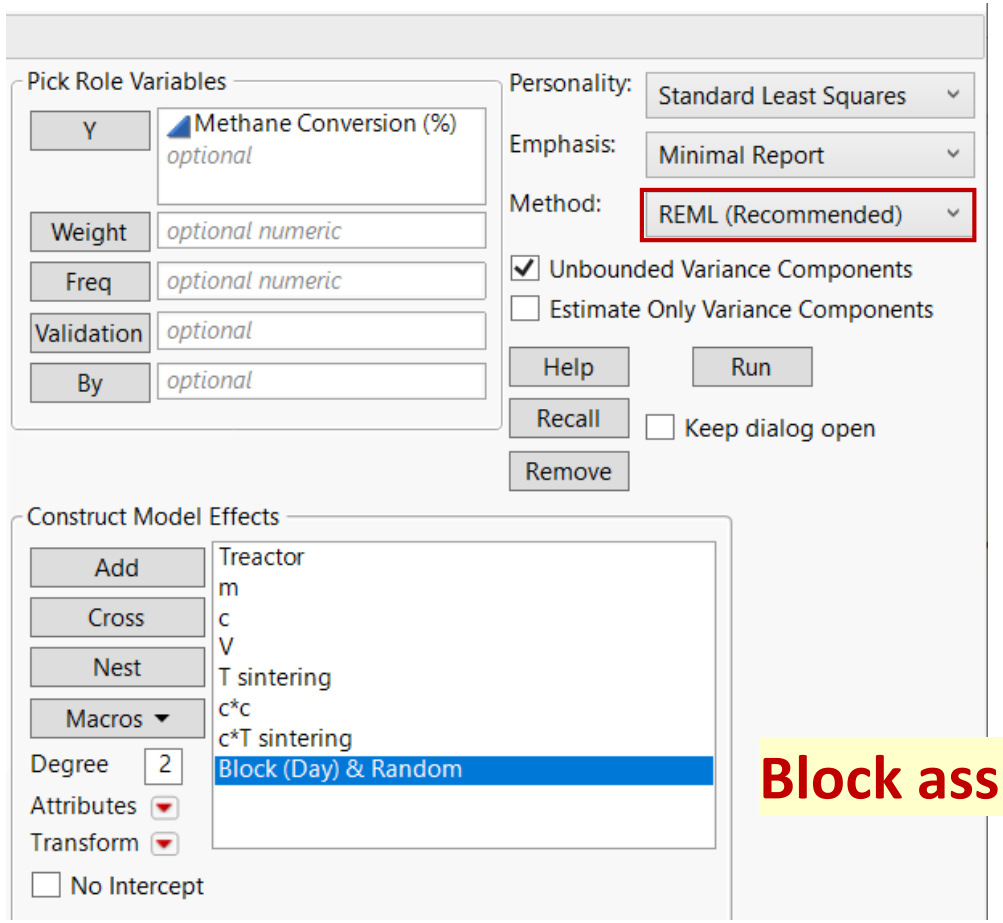
Assign Block (Day) as Random Effect

Significant Fixed Block effects

Analysis Custom DOE Results

Analysis strategy

2. Standard Least Squares REML Method



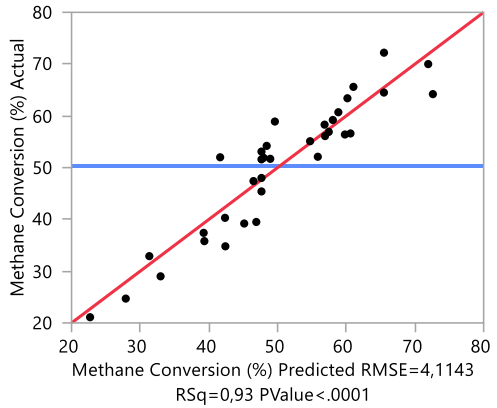
Remove day-to-day time variation from between response random error

Block assigned as random effect

Analysis Custom DOE Results

Results Standard Least Squares REML Method

Actual by Predicted Plot



Model OK

Summary of Fit

RSquare	0,931812
RSquare Adj	0,914133
Root Mean Square Error	4,11426
Mean of Response	50,29143
Observations (or Sum Wgts)	35

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	145,99185	42,37604	20,16	3,45	0,0025 *
Treactor	0,2671839	0,03037	19,7	8,80	<,0001 *
m	5,8902752	1,740159	19,98	3,38	0,0029 *
c	-0,323001	0,09053	19,67	-3,57	0,0020 *
V	-0,143749	0,032017	21,97	-4,49	0,0002 *
T sintering	-0,276667	0,027107	20,7	-10,21	<,0001 *
(c-30)*(c-30)	0,0549313	0,014884	20,15	3,69	0,0014 *
(c-30)*(T sintering-1178)	-0,009245	0,003777	24,73	-2,45	0,0218 *

All five main continuous effects significant!

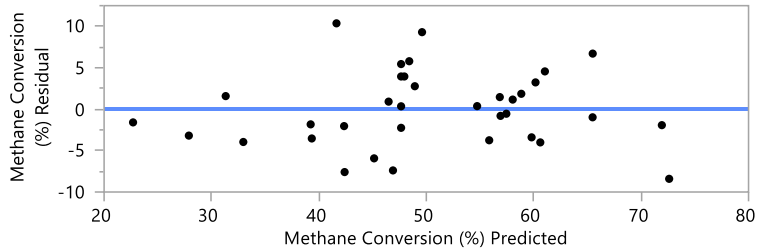
Low correlation between interaction effects → no need for augmenting custom DOE

Non Orhogonal DOE → Good choice!

Effect Summary

Source	LogWorth	PValue
T sintering	8,804	0,00000
Treactor	7,530	0,00000
V	3,738	0,00018
c*c	2,843	0,00143
c	2,706	0,00197
m	2,531	0,00295
c*T sintering	1,661	0,02184

Residual by Predicted Plot



REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Wald p-Value	Pct of Total
Block (Day)	0,4765463	8,0665623	6,6876256	-5,040943	21,174068	0,2277	32,274
Residual		16,927133	5,4985201	9,7841615	36,149497		67,726
Total		24,993695	7,5673605	14,921854	50,238961		100,000

?

Random block effect captures > 30% of total variation

-2 LogLikelihood = 229,43685367

Note: Total is the sum of the positive variance components.

Total including negative estimates = 24,993695

Analysis Custom DOE Results

Block (Day) Random (REML) vs. Block (Day) Fixed (OLS)

Term	Estimate	Prob>|t|	VIF
Intercept	145,99185	0,0025 *	.
Treactor	0,2671839	<,0001 *	1,0297121
m	5,8902752	0,0029 *	1,0081006
c	-0,323001	0,0020 *	1,0186032
V	-0,143749	0,0002 *	1,0297121
T sintering	-0,276667	<,0001 *	1,0081783
(c-30)*(c-30)	0,0549313	0,0014 *	1,0000777
(c-30)*(T sintering-1178)	-0,009245	0,0218 *	1,0345851

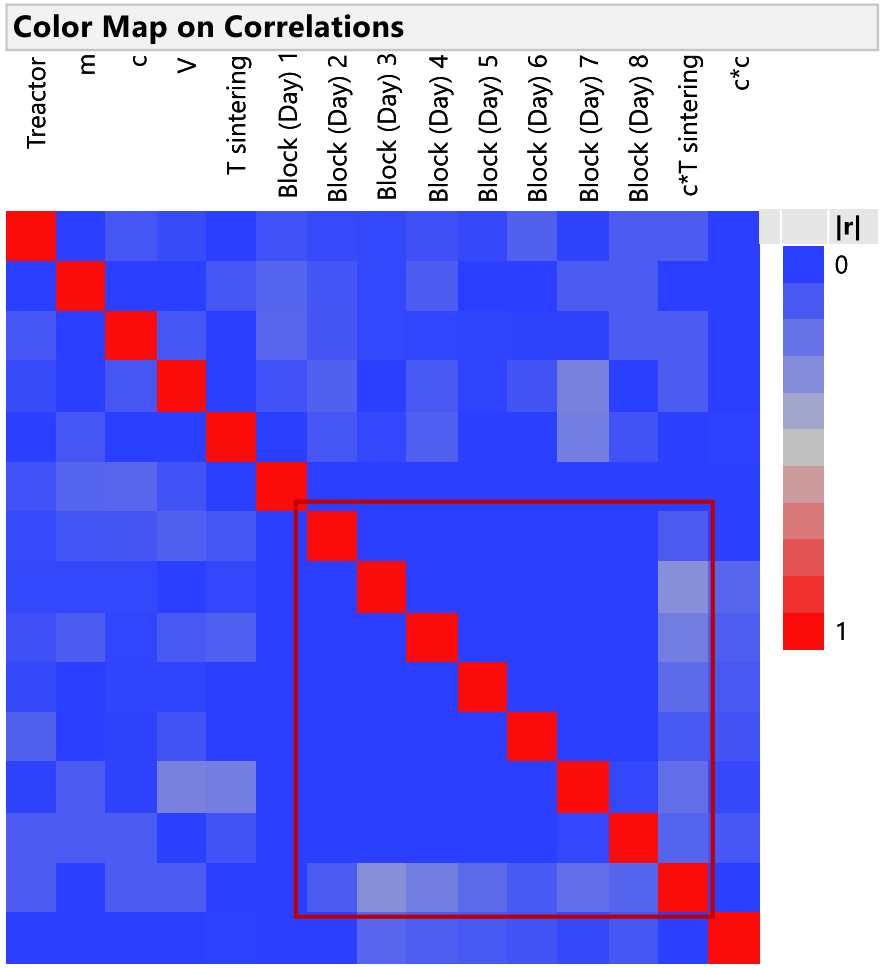
Term	Estimate	Prob>|t|	VIF
Intercept	132,48784	0,0039 *	.
Treactor	0,2640995	<,0001 *	1,0683285
m	6,2679259	0,0010 *	1,0208858
c	-0,311519	0,0017 *	1,0261372
V	-0,159341	<,0001 *	1,0884063
T sintering	-0,261776	<,0001 *	1,0817398
(c-30)*(c-30)	0,0562471	0,0007 *	1,0250152
(c-30)*(T sintering-1178)	-0,011368	0,0037 *	1,2779906
Block{2&7&8&6&3-5&1&9&4}	-2,994858	0,0010 *	1,3379991
Block{2&7-8&6&3}	-2,197699	0,0424 *	1,1583654
Block{5&1&9-4}	-3,368586	0,0163 *	1,451905

REML → more reliable model

Methane Conversion (%)

Analysis Custom DOE Results

Correlation Block (Day) Fixed (OLS)



Fixed Block Model

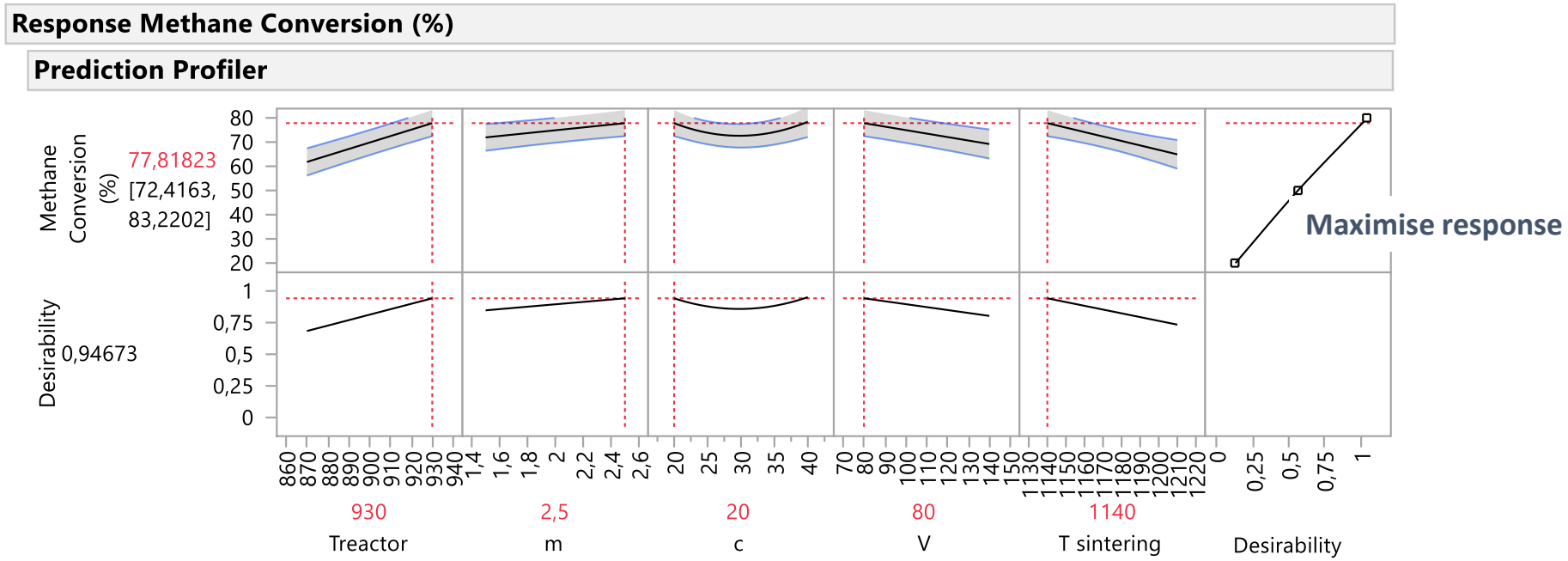
→ some correlation effects & Blocking factors

→ Increased VIF & lower efficiency

Analysis Custom DOE Results

Optimal process parameter settings Methane conversion

Specify Validation runs



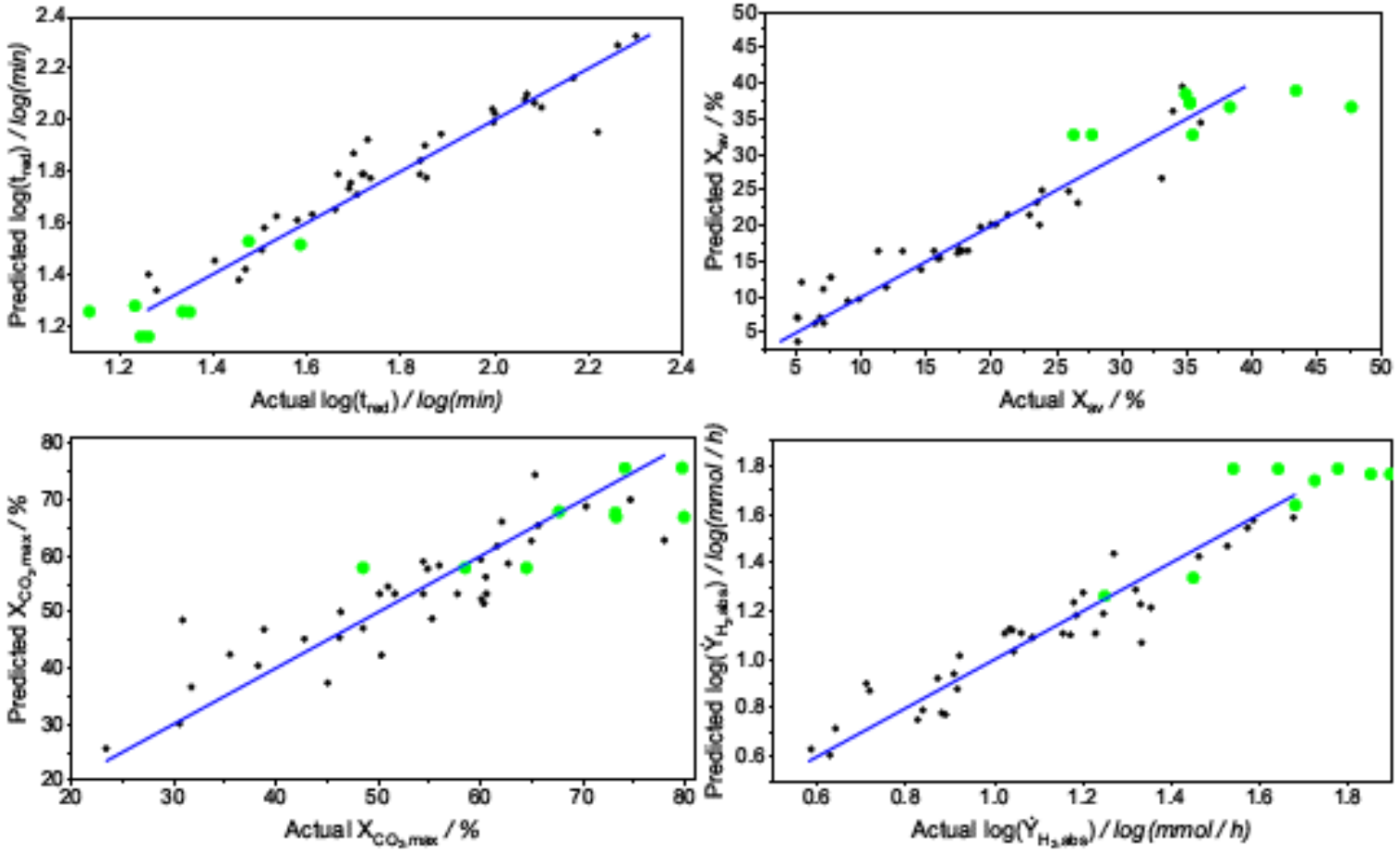
Optimal settings different (conflicting) for other responses → changed in validation runs

Optimal for other responses
Validation runs
Treactor = 930 °C

Optimal for other responses
Validation runs
T sintering = 1140 °C

Analysis Custom DOE Results

Results Standard Least Squares REML Method & Validation experiments



Fitting DOE & validation results OK!

USEFUL POLYNOMAL MODELS

SPECIFY DESIGN SPACE → OPTIMAL CHEMICAL LOOPING PERFORMANCE

CONCLUSION DOE STUDY

“It is very interesting to know that such a complex process, which is a fluidized-bed reactor, can be optimized utilizing a design of experiments approach”

Yoran De Vos

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