





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

Dr. Frank Deruyck

HOGENT University of Applied Sciences and Arts

• Dr. Yoran De Vos

VITO Research Mol Antwerp

• Dr. Peter Ohlemüller

TU Darmstadt

• Prof. Dr. Ir. An Verberckmoes Ghent University

Chemical looping

Partial oxidation hydrocarbons in fluidized bed reactor → Synthesis Gas



 $CO + 2H_2 \rightarrow$ Chemicals

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

 H_2O Oxidizing agent \rightarrow air & CO_2 also possible

Chemical Looping Steam Reforming



No dilution produced gases by air N₂ Lower gas separation costs during postprocessing Easier separation of CO₂ by-product

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

MODEL $Y_i = f(X_i)$

Response variables Y_i

- The time until the OC was completely reduced, $t_{\rm red}$ Minimise
- The average conversion of methane, $X_{\rm av}$

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

Input variables X_i





 $m_{\rm OC}$

X2

CCH₄

X3

 $T_{reactor}$

XI

T_{sintering} Size

x6

XS

[°C]

 V_{total}

X4

Plate

X7 (



7 controllable process parameters max 4 runs/day + blocking factor "Day"

2-level categorical



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

- **Sequential DOE Strategy**
- **1. D-Optimal Screening DOE**

Non Orthogonal DOE Blocked DSD or Custom DOE

- Estimate pure main effects, quadratic parameters
- 2^{nd} order interactions \rightarrow limited alias/correlation
- (!) # experiments < 40 9 10 days & max 4 runs/day
- No option \rightarrow fractional 2⁷⁻³ resolution IV + center/axial runs
- 2. Response Surface Model (RSM)
- Full quadratic polynomial model → Response optimization Augment Screening DOE with limited extra runs

Blocked Definitive Screening Design (DSD)

🔯 DOE - Definitive Screening Design 3 - JMP Pro

File Edit Tables Rows Cols DOE Analyze Graph Tools View Window Help

 Definitive Sc 	Definitive Screening Design							
Responses								
Factors								
Name	Role	Values						
X 3	Continuous	-1	1	~				
X 4	Continuous	-1	1					
X 5	Continuous	-1	1					
1 X6	Categorical	L1	L2					
1 X7	Categorical	L1	L2	\sim				

Design Options

O No Blocks Required

Number of Extra Runs 8

Add Blocks with Center Runs to Estimate Quadratic Effects

Add Blocks without Extra Center Runs

Number of Blocks



Make Design

Blocked Definitive Screening Design (DSD)

۷ 🔍									
	Block	X1	X2	Х3	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	•

Color Map on Correlations Blocked Definitive Screening Design |r| Main efects +/-100% pure 0

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

R < 0,6 → acceptable

Custom Design

🛛 💌 Custom Design

Responses

⊿ Factors

Add Factor 🔻	Remove	Add N Factors 1				
Name		Role	Changes	Values		
X 3		Continuous	Easy	-1	1	\sim
X 4		Continuous	Easy	-1	1	
X 5		Continuous	Easy	-1	1	
✓ X6		Categorical	Easy	L1	L2	
✓ X7		Categorical	Easy	L1	L2	\sim

Define Factor Constraints

None

- Specify Linear Constraints
- Use Disallowed Combinations Filter
- Use Disallowed Combinations Script

⊿ Model

Main Effects	Interactions 💌	RSM	Cross	Powers - Remove Term			
Name			E	Estimability			
X5		Necessary					
X6			N	Necessary			
X7			N	Necessary			
X1*X1			N	Necessary			
X2*X2			N	Necessary			
X3*X3			N	Necessary			
X4*X4		Necessary					
X5*X5			N	Necessary	~		

Alias Terms		
Main Effects Interactions 🔻	RSM Cross Powers - Remove Term	
Name		
X1*X2		\sim
X1*X3		
X1*X4		
X1*X5		
X1*X6		
X1*X7		
X2*X3		
X2*X4		\sim

⊿ Design Generation

Group runs into random blocks of size: 4

Number of Center Points:4Number of Replicate Runs:0

Number of Runs:

Minimum	18
Default	24
User Specified	36
Make Design	

Custom Design

۲ 💌									
	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	•

Color Map on Correlations

Custom Design 36 runs



+/- pure main effects

|r| 0

> Compared to DSD → quadratic effects less correlated

R < 0,6 → acceptable

Compare designs Custom DOE vs. Blocked DSD DOE

Diagnostics

esign Ev	aluation		Poor power quad
Powe	er Analysis		8. interaction offe
ignifican	ce Level 0,05		
Anticipate	d RMSE		
	Anticipated	Custom Design	Blocked Definitive
[erm	Coefficient	36 runs Power	Screening Design Power
ntercept	1	0,507	0,223
(1	1	0,992	0,970
(2	1	0,991	0,970
(3	1	0,986	0,970
(4	1	0,992	0,970
(5	1	0,962	0,970
(6	1	0,995	0,984
(7	1	0,998	0,984
(1*X1	1	0,698	0,108
(2*X2	1	0,637	0,081
(3*X3	1	0,617	0,107
(4*X4	1	0,667	0,057
(5*X5	1	0,639	0,067
(1*X2	1	0,894	0,424
(1*X3	1	0,828	0,288
(1*X4	1	0,687	0,286
(1*X5	1	0,791	0,313
(1*X6	1	0,720	0,156
(1*X7	1	0,950	0,145
(2*X3	1	0,874	0,123

0,80 0,60 0,40 0,20



Term

Compare designs Custom DOE vs. Blocked DSD **DOE Diagnostics**







Predictor Screening

	М	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				
с	47,448	0,0312		7				
Size	42,507	0,0279		8				

Significant random day-to-day variation!

- 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 Analysis strategy
- Stepwise forward Regression → RSM "Day" = block fixed effect Screen out significant effects
- 2. REML → Final RSM "Day" = random block effect

Response Methane Conversion (%)

Effect Summary

Size*Plate .	Source	LogWorth					PValue																																																																																																																																																																								
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REML → Backward regression 33 effects?



Stepwise Forward REML regression not possible?

REML Variance Component Estimates

Random		Var				Wald p-	
Effect	Var Ratio	Component	Std Error	95% Lower	95% Upper	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

Analysis strategy

1. Stepwise Regression

Fit Model - JMP Pro		- 🗆 ×	
 Model Specification 			
Select Columns	Pick Role Variables	Personality: Stepwise ~]
17 Columns	Y AMethane Conversion (%)	Help	
■ m OC ■ C CH4	Weight optional numeric	Recall Keep dialog open	
✓ Vtotal ✓ T sintering I. Size	Freq optional numeric Validation optional		
Il. Plate Time reduction Conv. @CO2max	By optional		
Sel. H2 @CO2max Sel. CO @CO2max	Construct Model Effects		
Y H2 @CO2max Y CO @CO2max	Cross Vtotal*Size		
	Nest Treactor*Plate m OC*Plate C CH4*Plate		
	Macros Vtotal*Plate Degree 2 Vtotal*Plate		
	Attributes Transform Size*Plate Block (Day)		Block (Day) = fixed effective
	No Intercept		

Analysis strategy

1. Stepwise Regression

Pick Role Variables Personality: Stepwise Fit for Methane Conversion (%) Standard Least Squares Methane Conversion (%) V Stepwise Regression Control Emphasis: Effect Screening optional Stopping Rule: Make Model Enter All Minimum AICc \sim Help Run Weight optional numeric Remove Al Run Model Direction: Recall optional numeric Freq Keep dialog open Forward \sim optional Remove Validation Rules: Combine Bv optional Go Stop Step Construct Model Effects Treactor Add m All 5 main continuous effects significant Cross С V Nest T sintering **Significant effects** c*c Macros c*T sintering Block (Dav){2&7&8&6&3-5&1&9&4} Degree 2 Block (Dav){2&7-8&6&3} Attributes 🕞 Block (Day) {5&1&9-4} Transform 💌 Assign Block (Day) as Random Effect Significant Fixed Block effects

Same results with "All Possible Models"

Analysis strategy

2. Standard Least Squares REML Method

Pick Role Va	riables	Personality:	Standard Least Squares v			
Y	Methane Conversion (%) optional	Emphasis:	Minimal Report v			
Weight	optional numeric	Method:	REML (Recommended) ~			
Freq	optional numeric	Unbounded Variance Components				
Validation	optional	L Estimate	Only Variance Components			
Bv	optional	Help Run				
		Recall	Keep dialog open			
		Remove				
Construct M	odel Effects					
Add	Treactor					
Cross	c m					
Nest	V T sintering					
Macros	✓ C*C					
Degree	2 C*T sintering		Dississe			
Attributes			BIOCK as			
Transform	▼					
No Inter	rcept					

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

Block assigned as random effect

Results Standard Least Squares REML Method

Actual by Predicted Plot



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
с	2,706	0,00197
m	2,531	0,00295
c*T sintering	1,661	0,02184

Residual by Predicted Plot



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
с	-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

REML Variance Component Estimates

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

-2 LogLikelihood = 229,43685367

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

Total including negative estimates = 24,993695

All five main continuous effects significant! Low correlation between interaction effects \rightarrow no need for augmenting custom DOE

Non Orhogonal DOE \rightarrow Good choice!

Value

Random block effect **Pct of Total** captures > 30% of total 32,274 67,726 variation 100.000

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

Term	Estimate	Prob> t	VIF	Term	Estimate	Prob> t	VIF
Intercept	145,99185	0,0025 *		Intercept	132,48784	0,0039 *	
Treactor	0,2671839	<,0001 *	1,0297121	Treactor	0,2640995	<,0001 *	1,0683285
m	5,8902752	0,0029 *	1,0081006	m	6,2679259	0,0010 *	1,0208858
С	-0,323001	0,0020 *	1,0186032	С	-0,311519	0,0017 *	1,0261372
V	-0,143749	0,0002 *	1,0297121	V	-0,159341	<,0001 *	1,0884063
T sintering	-0,276667	<,0001 *	1,0081783	T sintering	-0,261776	<,0001 *	1,0817398
(c-30)*(c-30)	0,0549313	0,0014 *	1,0000777	(c-30)*(c-30)	0,0562471	0,0007 *	1,0250152
(c-30)*(T sintering-1178)	-0,009245	0,0218 *	1,0345851	(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}

Block{5&1&9-4}

-2,197699

-3,368586

0.0424 * 1.1583654

1,451905

0,0163 *

REML → more reliable model Methane Conversion (%)

Correlation Block (Day) Fixed (OLS)



Fixed Block Model

- \rightarrow some correlation effects & Blocking factors
- → Increased VIF & lower efficiency

Optimal process parameter settings Methane conversion

Specify

Validation runs



Results Standard Least Squares REML Method & Validation experiments



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

Supervisors: Prof. Dr. Ir. An Verberckmoes, Prof. Dr. Pascal Van Der Voort, Prof. Dr. Isabel Van Driessche, Dr. Marijke Jacobs, Frans Snijkers

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