

Rubber Compounding Asia
Bangkok, March 2012
Organized by TechnoBiz Communications Co, Ltd.



Compound Development

**Advantage of Compound Development
with the
PC-Program “GrafCompounder”**

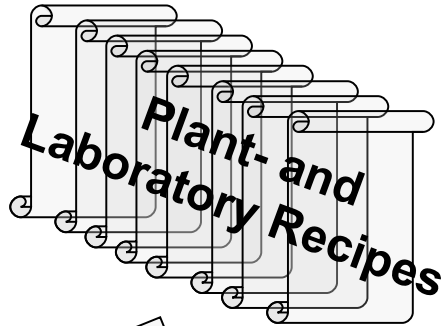
Dr. Hans-Joachim Graf
www.hans-joachim-graf.com

Compound Development

➔ Advantage of a PC-Program

- Motivation for Program Development
- Description of the GrafCompounder?
- Comparison with Statistic Experimental Design (DoE)
- Combination of Grafcompounder with DoE
- Advantages / Summary

Motivation for Program Development



**Recipe is used 1 Time
per
Project / Evaluation**



**Reinvention Time*)
~ 1- 2 Jahre!**

**) personal Estimation*

**Mid size - / Large company:
Recipes in use ~ 500 – 2000
Laboratory recipes ~ 1000/year**

***Cost of Recipe
Development in a
Laboratory
~ 500 US\$/Recipe
=
Invest of 500.000 US\$/year***

Motivation for Program Development



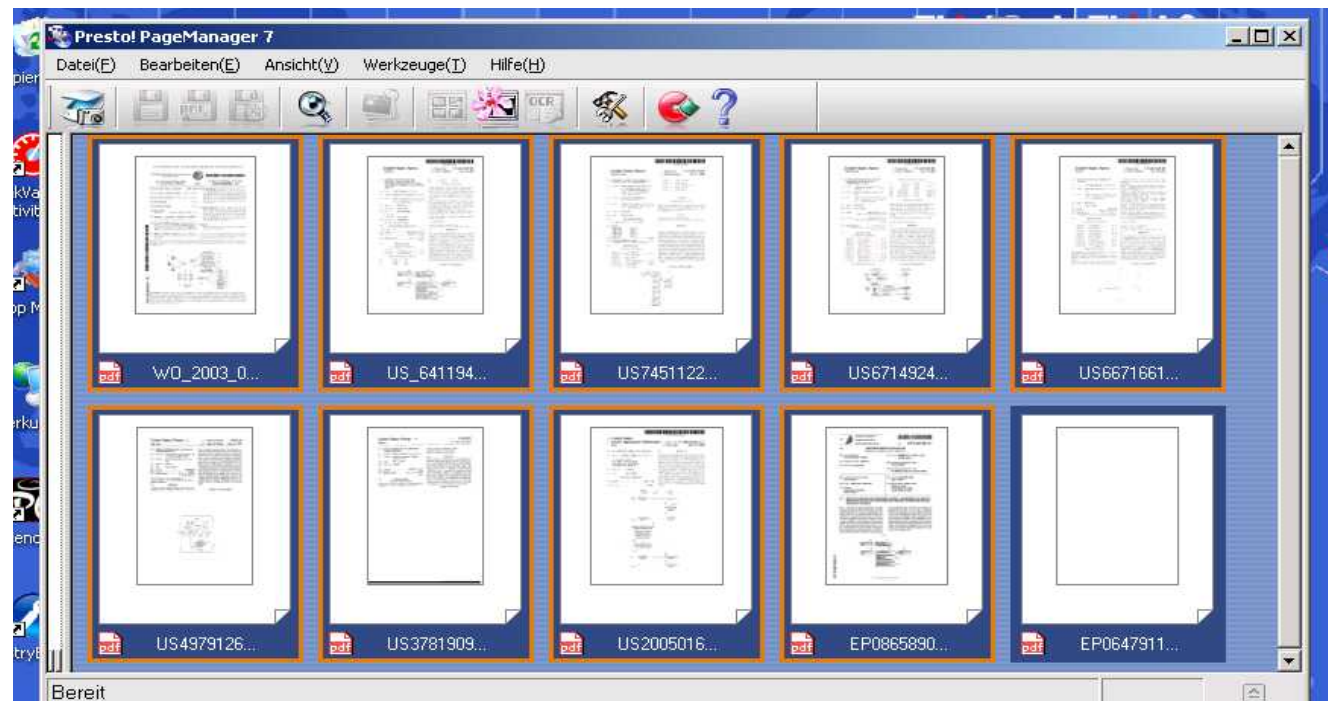
➔ Question:

- **Why we can hardly take Compound Databases as working capital, Saving time and effort in our daily work?**
 - **Avoiding reinvention**
 - **Increase our compounding knowledge.**
 - **Gaining room for really new ideas in compound development**

Motivation for Program Development



- Compound database is a kind of happen stance data
- Program developments and patents were dealing with “Neuronal Network Algorithmen” to create recipes from compound databases.



Motivation for Program Development



➔ Patent EP 0865 890 A1 (Bridgestone) is dealing with compounds used in tire manufacturing

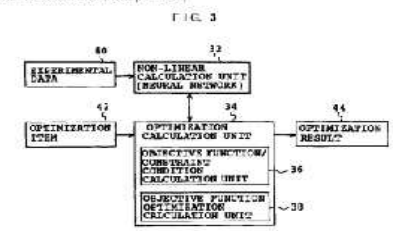
- Dependency of factor – response relationship with none linear regression equation.
- Usage of a function to determine boundary conditions.
- Identification of a compound with targeted properties.

 Europäisches Patentamt European Patent Office Office européen des brevets		 (11) EP 0 865 890 A1
EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC		
(43) Date of publication: 23.09.1998 Bulletin 1998/39	(51) Int. Cl. ⁶ B29B 9/14, G06F 17/00, B29D 30/00	
(21) Application number: 97934747.3	(86) International application number: PCT/JP97/02784	
(22) Date of filing: 08.08.1997	(87) International publication number: WO 98/06550 (19.02.1998 Gazette 1998/07)	
(84) Designated Contracting States: DE ES FR GB IT	(72) Inventor: NAKAJIMA, Yukio Tokyo 197 (JP)	
(30) Priority: 08.08.1996 JP 210273/96	(74) Representative: Whalley, Kevin MARKS & CLERK, 57-60 Lincoln's Inn Fields London WC2A 3LS (GB)	
(71) Applicant: Bridgestone Corporation Tokyo 104 (JP)		

(54) **METHOD OF DESIGNING MULTICOMPONENT MATERIAL, OPTIMIZATION ANALYZER AND STORAGE MEDIUM ON WHICH MULTICOMPONENT MATERIAL OPTIMIZATION ANALYSIS PROGRAM IS RECORDED**

(57) A design of a material composed of a plurality of components can be performed with ease. In an optimization apparatus 30, a known compositional ratios and the like, and mechanical behaviors thereof are inputted by an experimental data input unit 40 and a learning is conducted in a non-linear calculation unit 32 in order to establish a corresponding relation between compositional ratios of multi-component materials and the like, and mechanical behaviors thereof as a conversion system based on a neural network. Ranges and the like constraining mechanical behaviors, such as a Young's modulus and the like which are to be optimized,

and compositional ratios and the like are inputted in an optimization item input unit 42, and a mechanical behaviors are predicted in an optimization calculation unit 34 from compositional ratios and the like of the multi-component materials using the optimization item and the conversion system of the calculation unit 32, and an objective function is optimized until the objective function, expressing the mechanical behaviors are converged. The optimized compositional ratio and the like of the multi-component materials is output from an optimization result output unit 44.




EP 0 865 890 A1

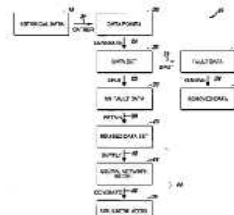
Motivation for Program Development



- ➔ The patent US 7541122B2 (Fa. Honeywell) deal with „empirical“ DoE with the help of neuronal network algorithm
 - Datenbase from historical compound data
 - Elimination of faulty data sets out of the data base
 - Calculation of a compound with the help of none linear neuronal network algorithm
 - Building of a equation for the simulation of the correlation between factors (compound ingredients) and responses (properties).



US 7541122B2

<p>(12) United States Patent Dietrich et al.</p> <p>(54) EMPIRICAL DESIGN OF EXPERIMENTS USING NEURAL NETWORK MODELS</p> <p>(65) Inventors: Paul E. Dietrich, Brooklyn Park, MN (US); Samit K. Meenan, Golden Valley, MN (US); Dinkar Mykassamany, Fridley, MN (US); Lewis E. Olson, Apple Valley, MN (US)</p> <p>(73) Assignee: Honeywell International Inc., Morrisville, NJ (US)</p> <p>(57) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 280 days.</p> <p>(21) Appl. No.: 11/994,317</p> <p>(22) Filed: Mar. 29, 2006</p> <p>(65) Prior Publication Data US 2007/0233633 A1 Oct. 11, 2007</p> <p>(51) Int. Cl. G06G 1/00 (2006.01) G06G 3/00 (2006.01) G06G 15/08 (2006.01) G06G 7/00 (2006.01) G06G 2/02 (2006.01)</p> <p>(52) U.S. Cl. 706/15</p> <p>(58) Field of Classification Search None See application file for complete search history.</p> <p>(56) References Cited U.S. PATENT DOCUMENTS 5,091,863 A 7/1992 Pavlovsk 5,461,809 A 10/1995 Arzabiz et al. 500/21 5,618,809 A 7/1997 Isankat et al. 5,684,340 A 11/1997 Iliu et al. 5,781,470 A 7/1998 Tsai 5,980,095 A 11/1999 Ishikawa; Ryano ... 707/119 6,161,754 A 12/2000 Rosenfeld et al. 706/121 6,209,712 B1 6/2001 Bokorovic et al. 706/21 6,353,804 A 3/2002 Hsu et al.</p>	<p>(19) Patent No.: US 7,451,122 B2</p> <p>(45) Date of Patent: Nov. 11, 2008</p> <p>6,411,955 B1 6/2002 Nakama 6,470,991 H1 8/2002 Sato 6,496,347 B1 12/2002 Chikara et al. 6,604,092 B1 8/2001 Steinet 6,666,617 H1 8/2001 Sato et al.</p> <p>(Continued)</p> <p>OTHER PUBLICATIONS Fault diagnosis in gas turbine engines using fuzzy logic Gwynne, D.; Moore, S.; Ball, P.; Mukawa, T.; Nandagopal, F.; Systems, Man and Cybernetics, 2003. IEEE International Conference on vol. 4, Oct. 5-8, 2003 pp. 3756-3762 vol. 4 *</p> <p>(Continued)</p> <p>Primary Examiner: Mitchell B. Holmes (74) Attorney, Agent, or Firm: Laurussia, Fisher & Lorenz, P.C.</p> <p>(57) ABSTRACT Methods and apparatus are provided pertaining to a design of experiments. The method comprises generating a data set from historical data, identifying and removing any bad data points in the data set so as to create a revised data set; supplying the data points from the revised data set into a nonlinear neural network model; and deriving a simulator model characterizing a relationship between the input variables and the output variables. The apparatus comprises means for generating a data set from historical data; means for identifying and removing any bad data points in the data set so as to create a revised data set; means for supplying the data points from the revised data set into a nonlinear neural network model; and means for deriving a simulator model characterizing a relationship between the input variables and the output variables.</p> <p>24 Claims, 7 Drawing Sheets</p> 
---	---

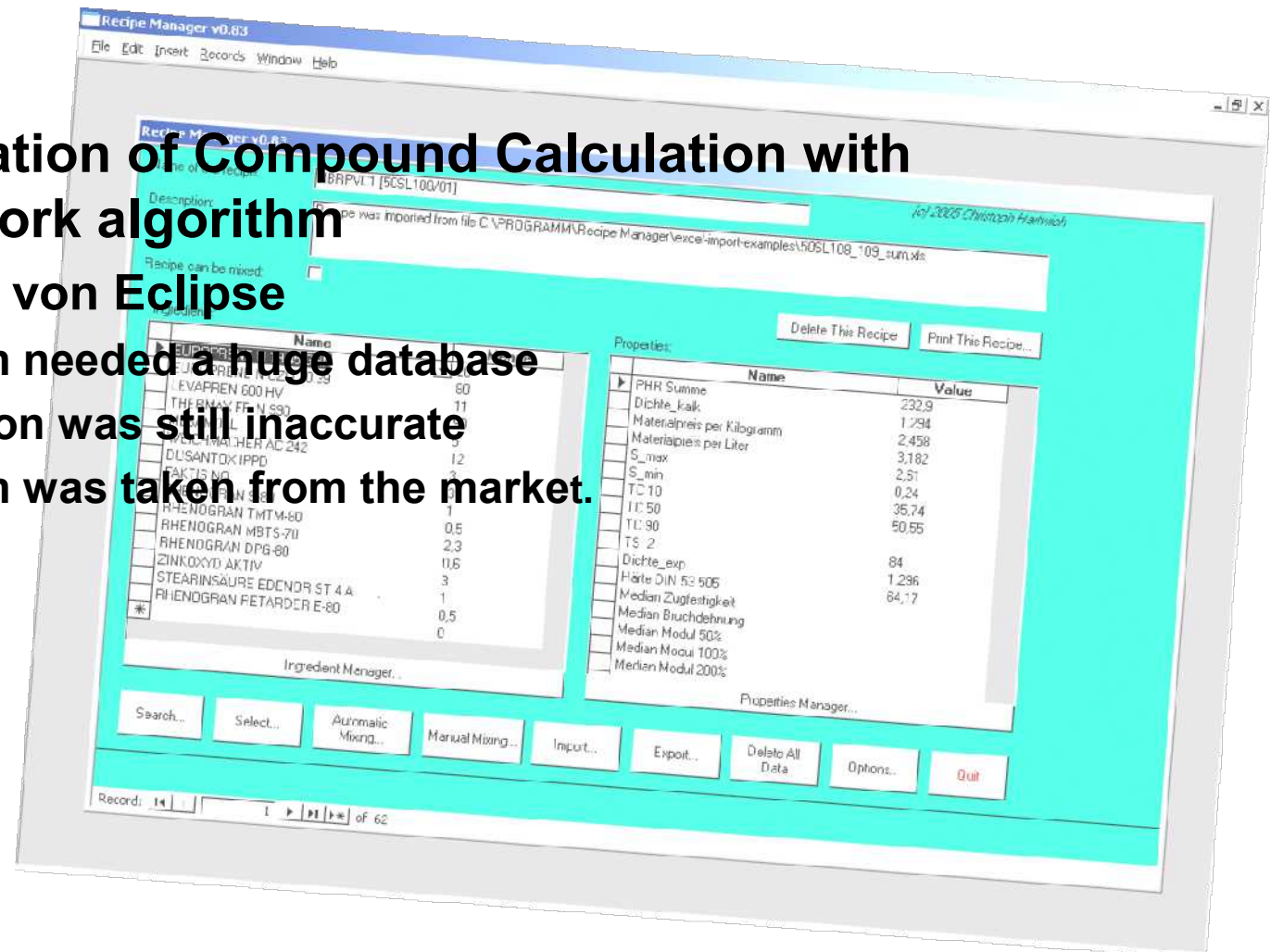
Motivation for Program Development



➔ Commercialisation of Compound Calculation with neuronal network algorithm

● CAD-CHEM von Eclipse

- Program needed a huge database
- Prediction was still inaccurate
- Program was taken from the market.



Motivation for Program Development

➔ **Statistic Experimental Design (DoE) allows a factor – response calculation with regression equations**

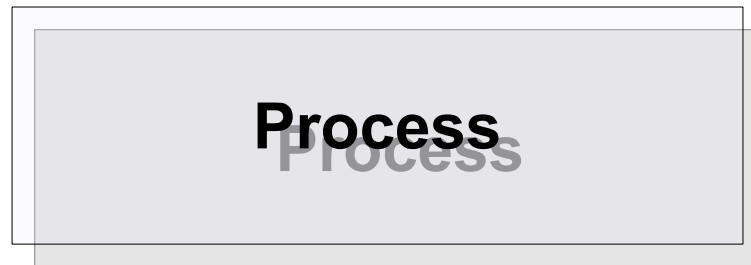
Influences:

Factors are varied

F_1 ➔

F_2 ➔

F_3 ➔



Effects:

Responses are measured

➔ R_1, R_2, \dots, R_n

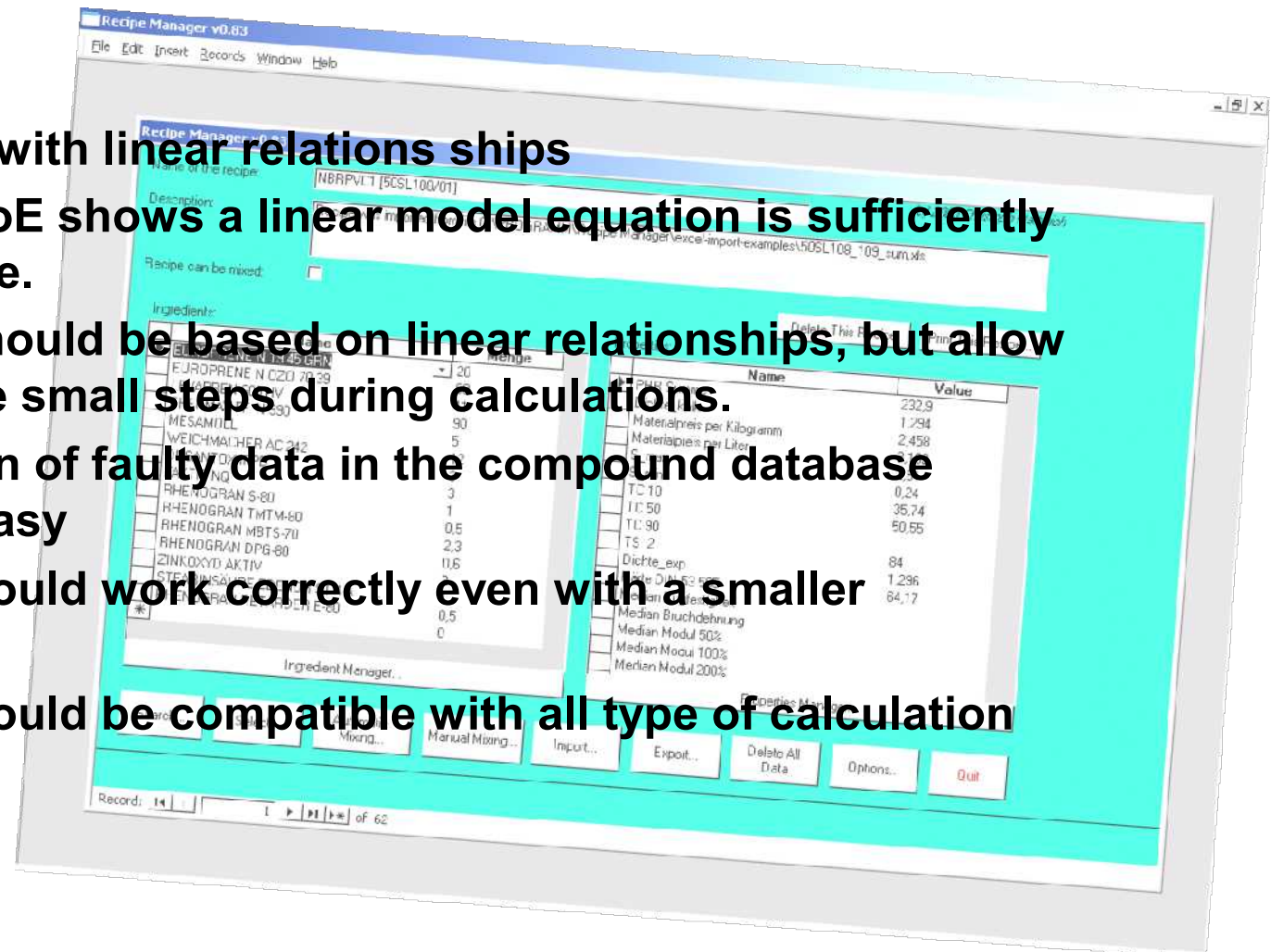
- ➔ **Objective of the Experiment should be the identification of the most important factors (F_1, \dots, F_n), to be able to measure Effects (Responses R_1, \dots, R_n) and to describe their dependency in a mathematical equation:**

$$R_{i(1 \dots n)} = f(A_0 + A_1 F_1 + \dots + A_n F_n + \dots)$$

Design Guide for GrafCompounder



- Calculation with linear relationships
 - Most DoE shows a linear model equation is sufficiently accurate.
 - Math should be based on linear relationships, but allow multiple small steps during calculations.
- Identification of faulty data in the compound database should be easy
- Program should work correctly even with a smaller database
- Program should be compatible with all type of calculation programs



Description of GrafCompounder



- ➔ **Analysis of a recipe database with Multiple Linear Iteration (MLI)**
 - **Search criteria manageable with different weights!**
 - **Recipe Selection (Exclusion of unwanted recipes during analysis)**
 - **Avoid Analysis of none compatible Polymers**
 - **Automatic an Manual Mode**
 - **Simulation of Blends of Compounds**
 - **Property Data should be from a trustworthy source, if not your own**

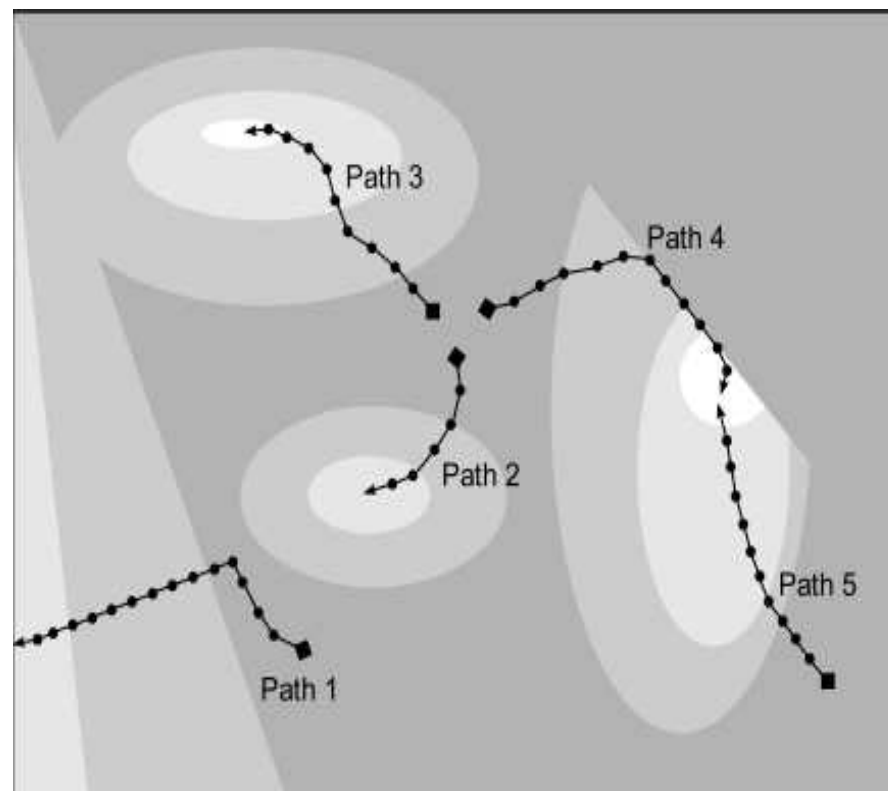
Description of GrafCompounder

➔ Analysis based on

- Measurables
- Targets
- Weights
- Rating functions shows the distance between values and target
- Iteration in small steps from different starting points
- Check of maximum agreement with the target

➔ Report of Results

- Recipe
- All calculable physical properties
 - Missing data left out
- Show all Recipes with their percentage used in an analysis



Description of GrafCompounder

➔ Working with the GrafCompounder

- Create a table via **Export** from **Desing Expert®**
- Assign the rows and columns
 - Recipes:
 - Ingredients:
 - Properties:

	Recipes:		
Ingredients:	CMPD1	CMPD2	CMPD3
XXX	XXX	XXX	XXX
Properties:			
XXX	XXX	XXX	XXX

Comparison DoE versus GrafCompounder

- ➔ **Testing the MLI-method a database is needed, which can be analyzed in different ways.**
 - **1. Example**
 - Oil / Filler DoE (with own Experiments)
 - Factors: Filler 1, Filler 2, Filler3 and Oil
 - **2. Example**
DoE published by DuPont Dow in 1998
 - Factors: ENB, DTDC, S, MBT, TiTBD, ZdiBC, DTP
- **Same Optimization criteria will be used in DoE Software (Design Expert®) and in GrafCompounder.**

Comparison DoE versus GrafCompounder



- **1. Example**
 - **Oil / Filler DoE (based on own Experiments)**
 - **Factors: Filler 1, Filler 2, Oil**

Comparison DoE versus GrafCompounder

➔ DoE with 4 Factors

Polymer used was Vistalon 8600

➔ Factor	Name	Units	Minimum	Maximum
● A	C6630	phr	60.00	95.00
B	CaCO3	phr	10.00	70.00
C	Clay	phr	10.00	50.00
D	Oil	phr	70.00	95.00

- A fractional factorial DoE with 11 compounds only!

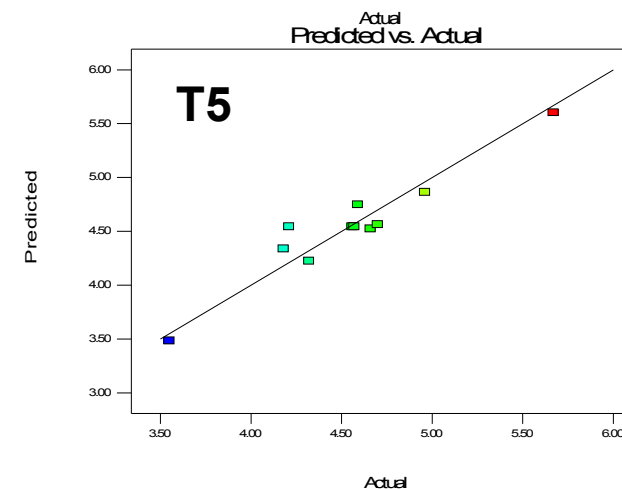
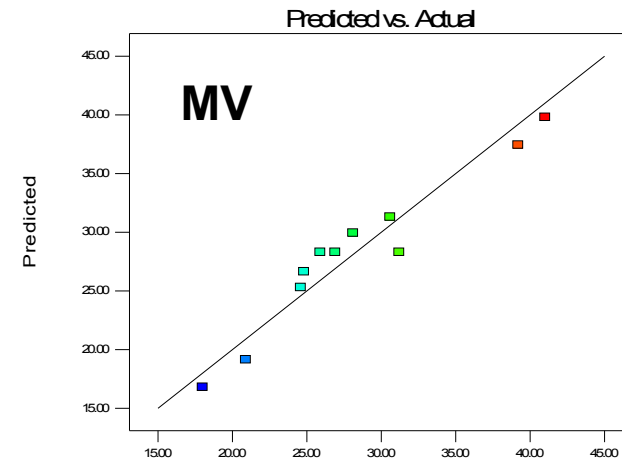
Comparison DoE versus GrafCompounder



➔ **Rheological Data are examined**

- **MV and T5 can be measured quite accurate.**

Both are significant with a linear model equation



Comparison DoE versus GrafCompounder

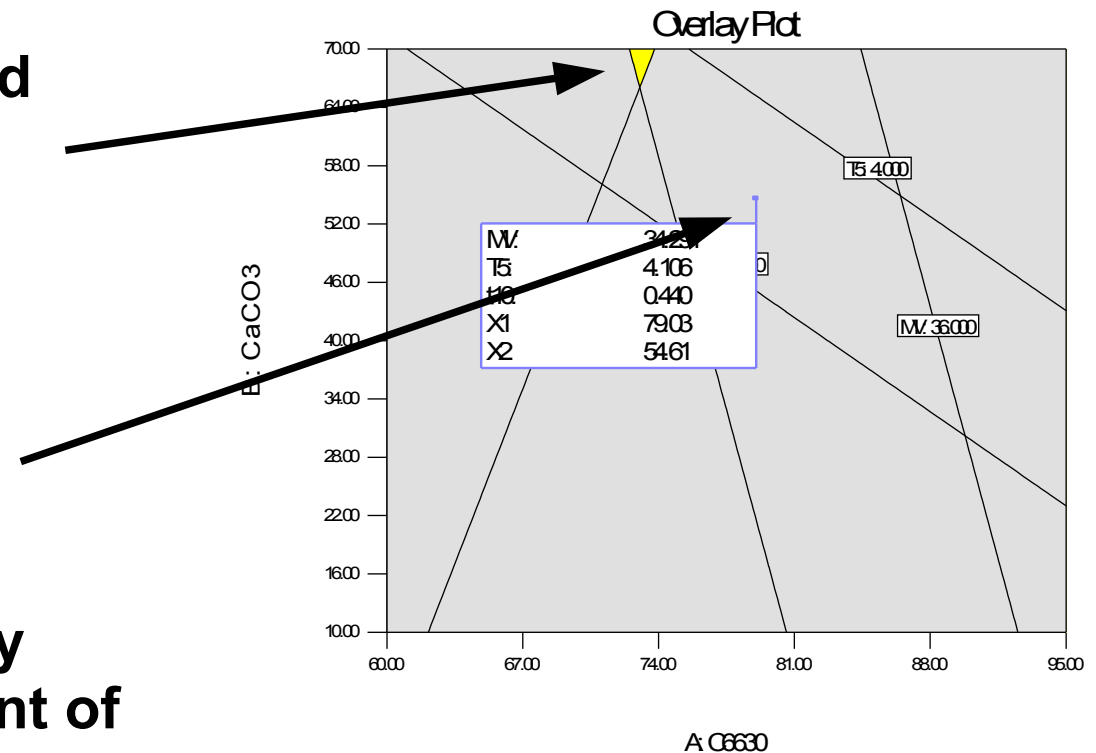


Ingredients	Unit	DoE Optimization	GrafCompounder
CB 6630	phr	73	79
CaCO ₃	phr	68	55
Clay	phr	39	39.5
Paraffinic Oil	phr	72	73
MV 120	MU	34	34.9
T5 (120°C)	min	4.04	4.2
t10 (170°C)	min	0.45	0.44

Comparison DoE versus GrafCompounder



- ➔ Optimization area calculated with Design Expert
- ➔ Solution given by GrafCompounder
- ➔ With an additional boundary condition: take same amount of CB 6630 similar to Optimization Value in Design Expert



Comparison DoE versus GrafCompounder



Ingredients	Unit	DoE Optimization	GrafCompounder	CI 95% Low - High	CI 95% Low-High
				DOE Prediction	Graf Compounder
CB 6630	phr	73	79		
CaCO3	phr	68	55		
Clay	phr	39	39.5		
Paraffinic Oil	phr	72	73		
MV 120	MU	34	34.9	30-36	31-35
T5 (120°C)	min	4.04	4.2	3.8-4.3	3.9-4.4
t10 (170°C)	min	0.45	0.44	0.42-0.48	0.41-0.47

Comparison DoE versus GrafCompounder

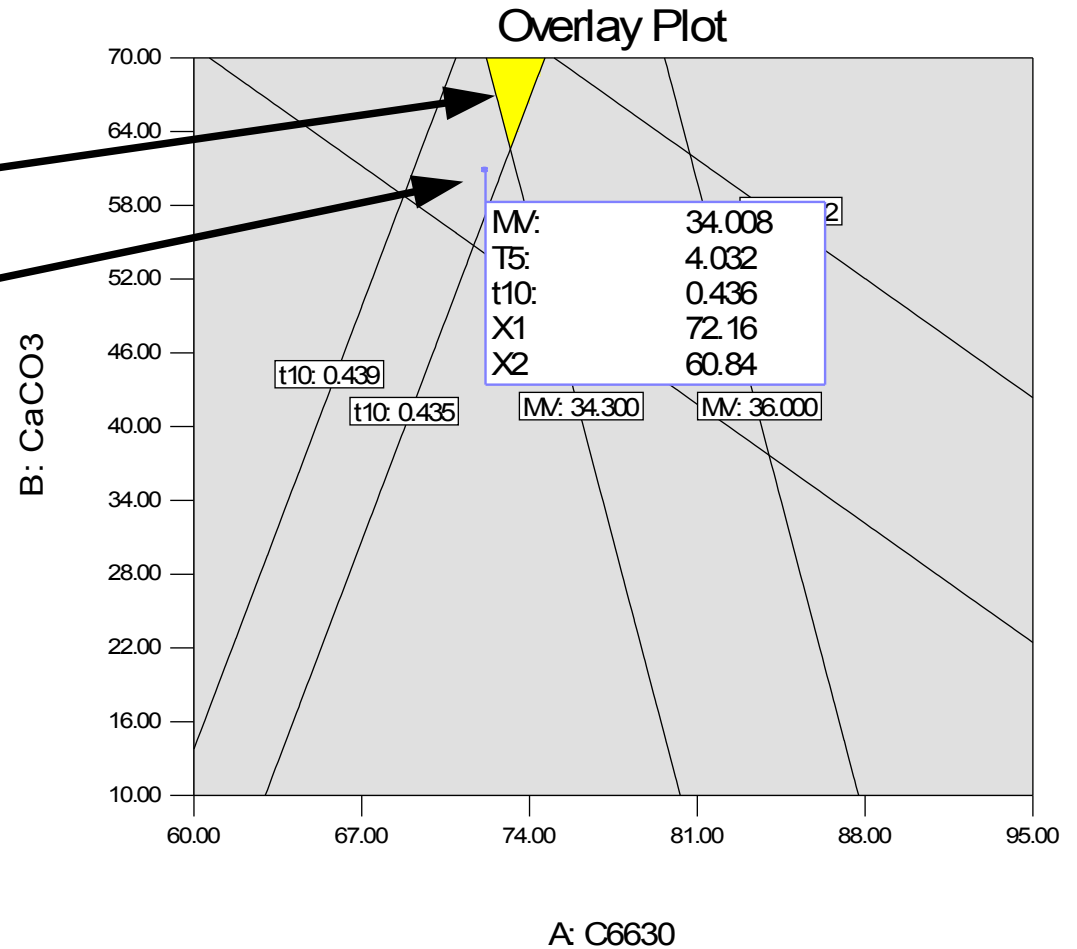


Ingredients	Unit	DoE Optimization	GrafCompounder
CB 6630	phr	73	73
CaCO3	phr	68	61
Clay	phr	39	32
Paraffinic Oil	phr	72	70
MV 120	MU	34	34.1
T5 (120°C)	min	4.04	4.1
t10 (170°C)	min	0.45	0.45

Comparison DoE versus GrafCompounder



- ➔ Optimization area calculated with Design Expert
- ➔ Solution given by GrafCompounder with the additional condition (CC 6630 – 73 phr)



Comparison DoE versus GrafCompounder



➔ What we have learned

- **Calculation with GrafCompounder and optimization result with Design Expert has some characteristic differences**
 - **GrafCompounder give one solution always**
 - **Design Expert provides an area, where you can identify a solution**
 - **With an additional boundary condition both solutions can be narrowed, that they fit into measurement error.**

Comparison DoE versus GrafCompounder



- **2. Example**
- **DoE published by DuPont Dow in 1998**
 - **Factors: ENB, DTDC, S, MBT, TiTBD, ZdiBC, DTP**
 - **DoE with 41 Experiments**

DoE Analysis and Result

➔ Tensile at break is significant with linear model

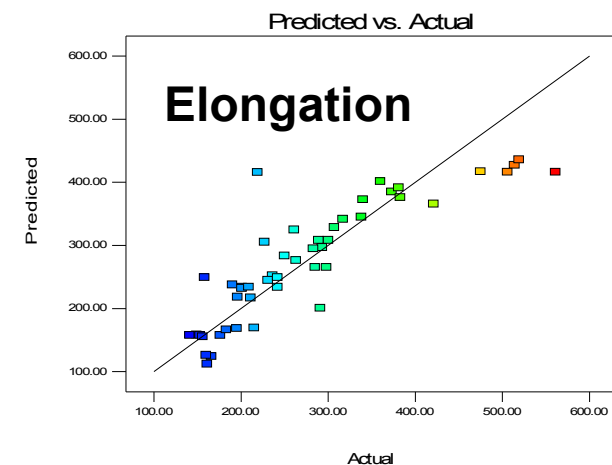
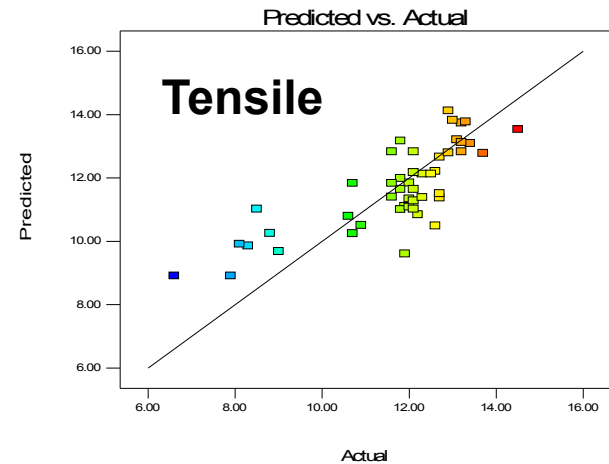
- Sulfur has larger influence followed by DTDC and TiBTD, but negative

➔ Elongation is significant with quadratic model, but linear model is a sufficient fit

- Sulfur has the largest influence followed by DTDC

➔ Hardness is sufficient significant with linear model as well

- Main influence Sulfur, DTDC

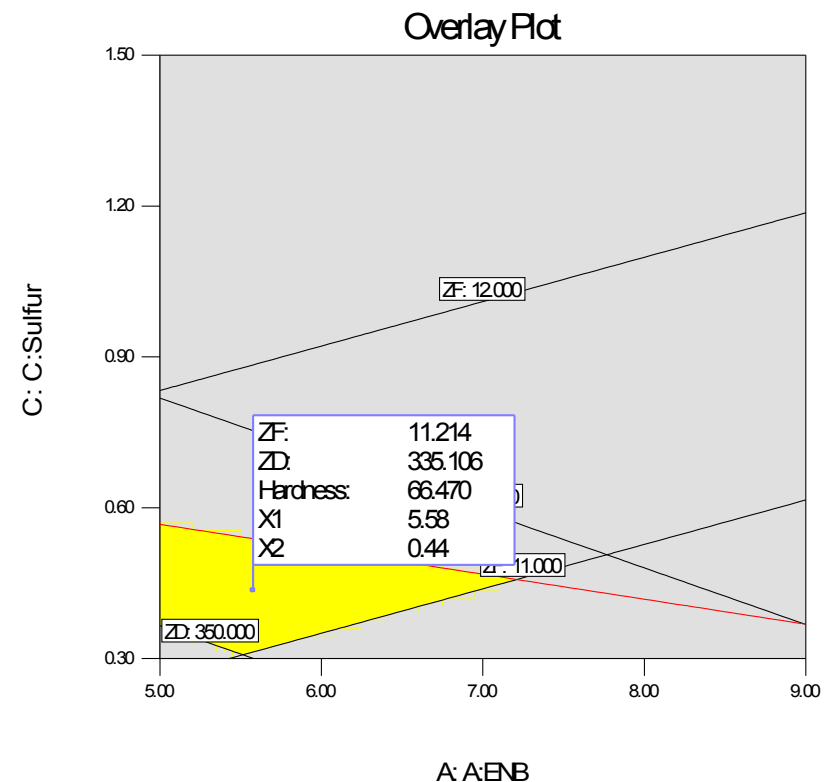


DoE Analysis and Result

➔ Selection of responses for the test with graphical optimization:

- Hardness
65°ShA - 70°ShA
- Tensile at break
11MPa – 12 MPa
- Elongation of Break
350 % - 400 %

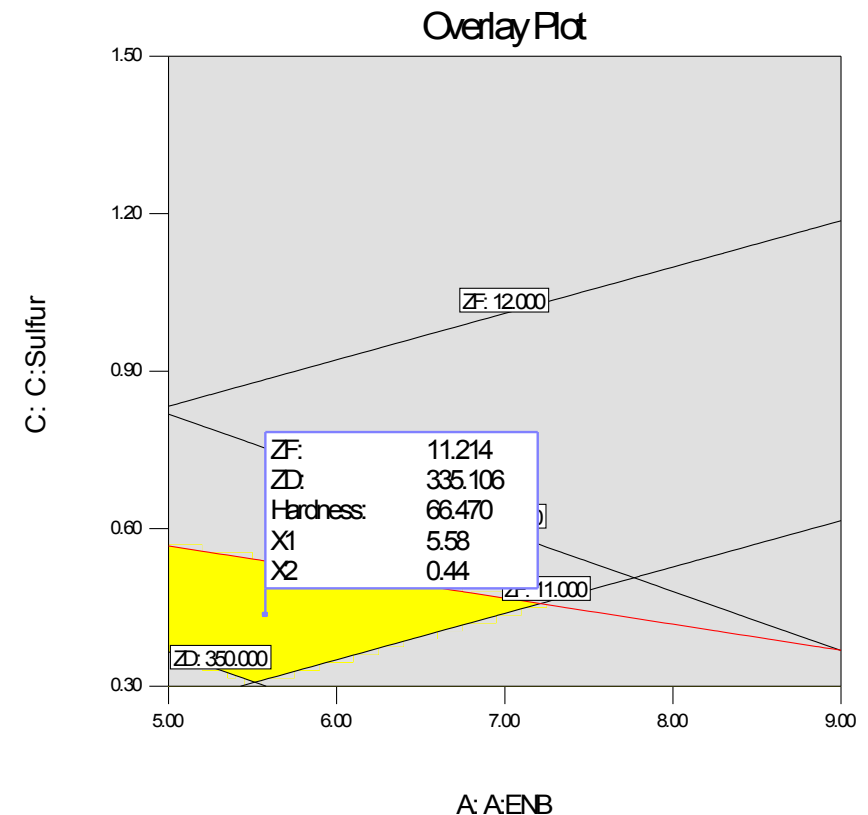
➔ Flag points to one solution



DoE Analysis and Result

➔ Factor values giving this result

- ENB: 5,58%
- Sulfur – 0.44 phr
- DTDC – 2.11 phr
- MBT – 1.00 phr
- TiBTD – 1.50 phr
- ZdiBC – 1.50 phr
- DTP – 1.50 phr



DoE Analysis and Result

➔ Analysis with point prediction results:

- ZF 11.2 MPa
- ZD 334 %
- Hardness 66.5°ShA

Factor	Name	Level
A	ENB	5.58
B	DTDC	2.11
C	Sulfur	0.44
D	MBT	1.00
E	TiBTD	1.50
F	ZDiBC	1.50
G	DTP	1.50

Analysis with GrafCompounder

- ➔ Paste table into Graf Compounder
- Select boundaries

GrafCompounder version 1.001

File Edit Help

Input data:

	Recipes:									
Ingredients:	cura Pro 1	cura Pro 2	cura Pro 3	cura Pro 4	cura Pro 5	cura Pro 6	cura Pro 7	cura Pro 8	cura Pro 9	cura Pro 10
Nordel P 4...		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Zinc Oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
CD N 65C	175.00	175.00	175.00	175.00	175.00	175.00	175.00	175.00	175.00	175.00
Sunpar 2280	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
B-DTDC	3.00	0.00	3.00	3.00	3.00	3.00	3.00	1.50	0.00	3.00
D-Sulfur	1.50	1.50	1.50	1.50	1.50	1.50	1.50	0.30	1.50	1.50
D-MBT	1.50	0.50	1.50	0.50	0.50	0.50	0.50	1.50	1.50	0.50
E-TBTD	0.00	3.00	3.00	3.00	3.00	3.00	3.00	1.50	3.00	3.00
F-ZDIBC	0.00	0.00	1.50	3.00	0.00	1.50	0.00	3.00	3.00	3.00
G-DIP	0.00	0.00	3.00	3.00	3.00	3.00	3.00	0.00	0.00	0.00
Properties:										
A:ENB	9.00	5.00	5.00	9.00	5.00	5.00	5.00	9.00	5.00	5.00
Units Mooney Peak	02.00	09.00	05.00	06.00	01.00	02.00	00.00	02.00	01.00	01.00
Units MI 1+4	61.00	68.00	65.00	49.00	61.00	71.00	69.00	68.00	67.00	67.00
Nrrr ML	1.00	1.10	1.10	0.90	1.00	1.10	1.10	1.00	1.00	1.20
mir. Is2	3.10	2.40	1.90	1.90	3.00	1.90	3.00	1.90	1.90	2.50
mir. Is90	20.90	13.90	13.30	8.60	13.50	15.10	6.40	9.30	10.70	10.70
Nrrr MH	8.50	6.90	3.90	9.30	8.20	6.70	5.40	8.50	3.90	3.90
MPa M 50	3.75	2.29	2.71	3.72	2.68	2.23	1.68	2.81	2.71	2.71
MPa M 100	7.56	5.49	5.59	8.32	6.09	5.19	3.50	6.69	7.15	7.15
MPa ZF	13.20	13.70	13.10	13.40	12.90	12.50	10.60	12.70	13.20	13.20
% ZD	176.00	263.00	211.00	156.00	215.00	261.00	373.00	190.00	183.00	183.00
Store A Hardness	75.00	68.00	72.00	72.00	72.00	69.00	53.00	71.00	72.00	72.00
% DS 24/100	44.50	49.60	43.60	38.40	36.20	32.60	32.60	30.20	36.40	36.40
% DS 24/125	69.00	65.90	61.00	58.70	67.30	54.50	50.70	56.80	55.70	55.70
24hr/150 CS 24/150	81.60	74.90	69.40	67.90	67.90	63.10	73.40	69.60	69.90	69.90
% Rebound	91.90	56.30	38.40	35.20	27.00	35.40	31.90	21.90	37.40	37.40
Unit I an delta	0.32	0.32	0.33	0.31	0.32	0.32	0.36	0.32	0.29	0.29
MPa M50 70/125	5.20	4.30	5.31	0.98	5.01	4.30	2.70	5.14	5.20	5.20

Criteria: From To Weight Trdcff

Output: Mixture

Recipe ratios in %:

Number format: 12345.67

Import input data from clipboard | Auto mix (overwrite mixture) | Auto mix (new mixture)

Analysis with GrafCompounder



➔ Paste table into GrafCompounder

- **Select boundaries**
- **ZF-MPa : 11.5-12.0**
- **ZD-% : 325-335**
- **H-°ShA : 65-67**

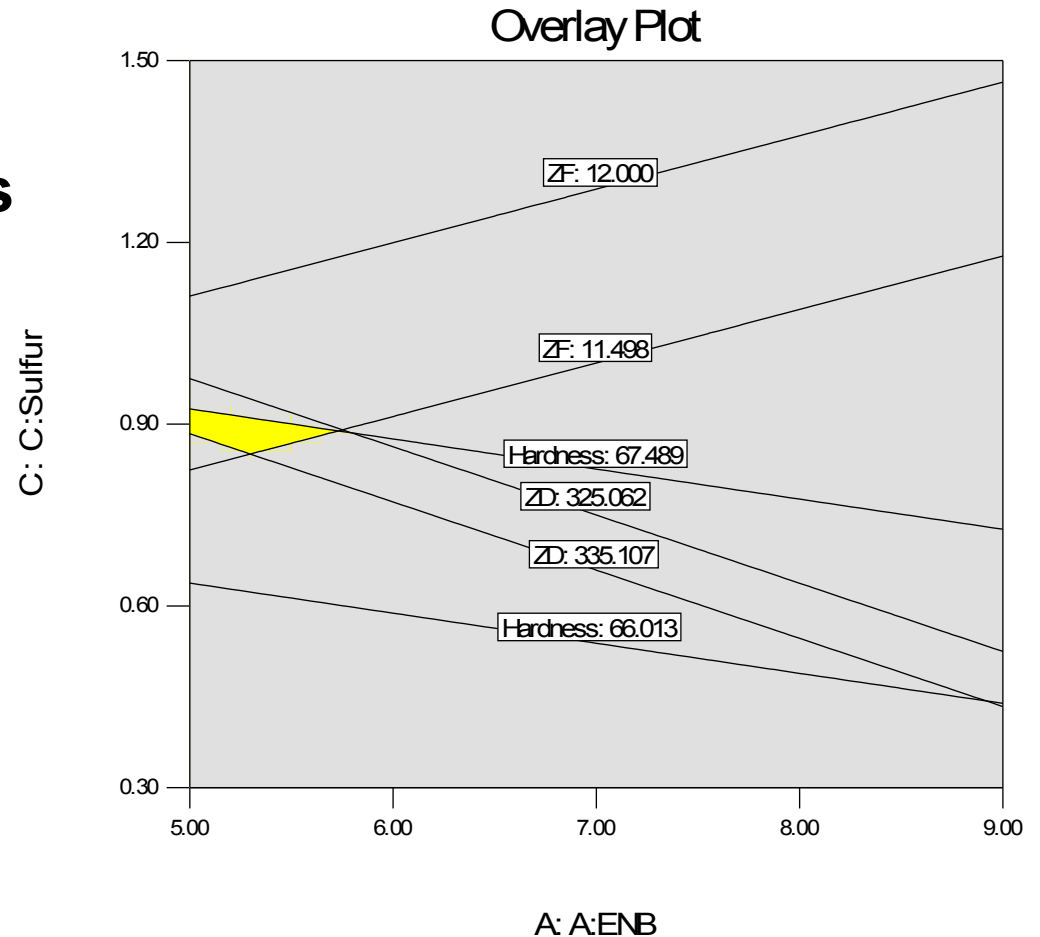
Ingredients	Result
B:DTDC	0.98
C:Sulfur	0.93
D:MBT	1
E:TiBTD	1.51
F:ZDiBC	1.33
G:DTP	1.45
ZF	11.5
ZD	325
Hardness	67

Analysis with Design Expert®



Run Optimization Graphical

- Select same boundaries
- ZF-MPa : 11.5-12.0
- ZD-% : 325-335
- H-°ShA : 65-67



Analysis with GrafCompounder



- ➔ **Boundary Conditions**
- **Select boundaries**
 - **ZF-MPa : 11.5-12.0**
 - **ZD-% : 325-335**
 - **H-°ShA : 65-67**

Ingredients	Result GrafCompounder	Result Design Expert®
ENB	6.5	5.45
C:Sulfur	0.93	0.88
B:DTDC	0.98	0.98
D:MBT	1	1
E:TiBTD	1.51	1.51
F:ZDiBC	1.33	1.33
G:DTP	1.45	1.44
ZF	11.5	11.5
ZD	325	330
Hardness	67	67.5

+) Note: Accelerators are preset!

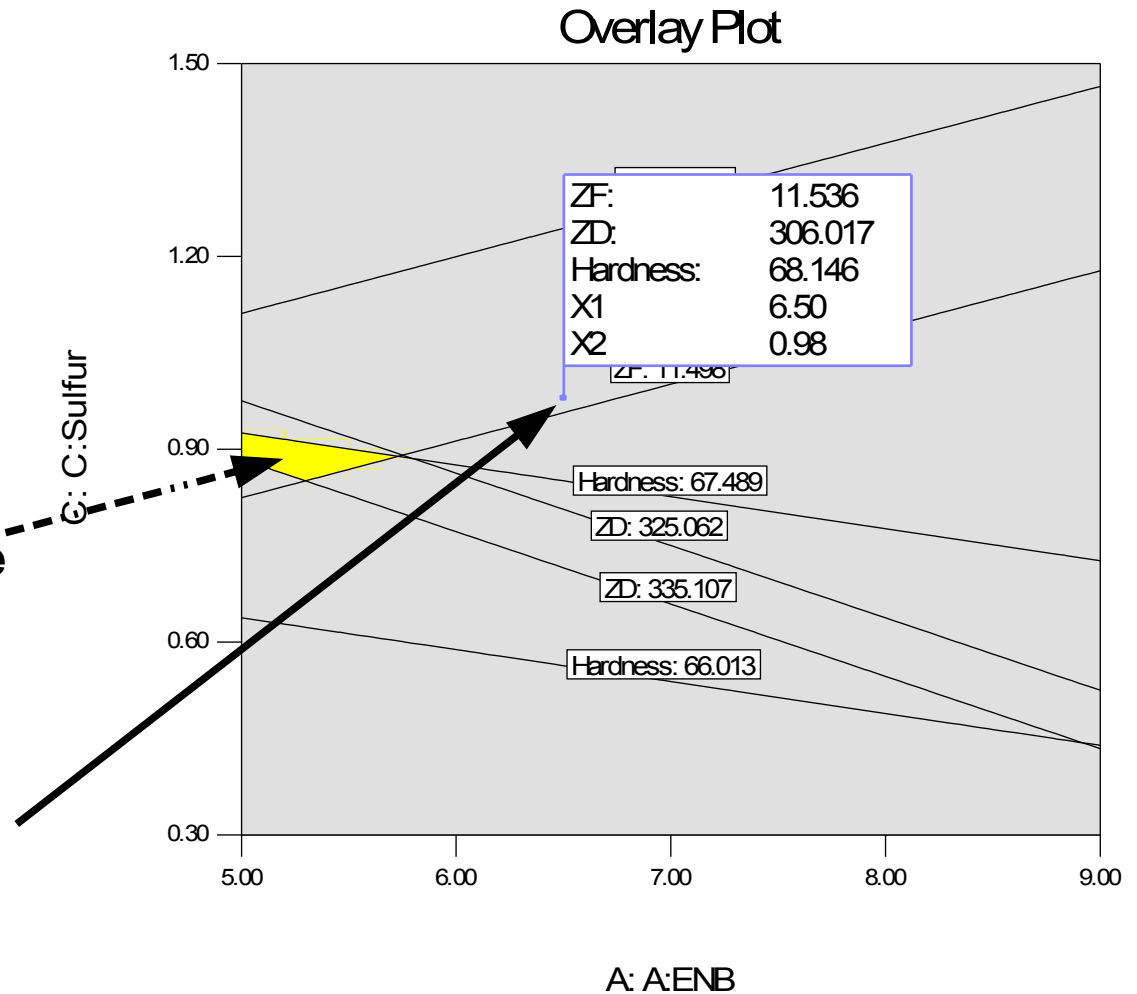
Compare Result Design Expert® vs GrafCompounder



➔ Boundary Conditions

- Select boundaries
- ZF-MPa : 11.5-12.0
- ZD-% : 325-335
- H-°ShA : 65-67

➔ The Design Expert optimization graph shows the location of the result as a yellow area, but GrafCompounder result is tagged with a flag.



Conclusion

- ➔ **Compounds in databases are type of happenstance data**
 - **Which can not analyzed with a systematic approach today**
 - **DoE in each case needs data based on a planned experiment.**
- ➔ **GrafCompounder allows to search a database for a possible solution using targets**
 - **At minimum you get an very good idea about the center point in a DoE**