Compound Development

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

Compound database is a kind of happenstance data. Program developments and patents were dealing with "Neuronal Network Algorithmen" to create recipes from compound databases.
Motivation for Program Development

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

Recipe is used 1 Time per Project / Evaluation

Reinvention Time*)
~ 1- 2 Jahre!

*) personal Estimation
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
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.
Motivation for Program Development

The patent US 7541122B2 (Fa. Honeywell) deal with „empirical“ DoE with the help of neuronal network algorithm

- Database from historical compound data
- Elimination of faulty data sets out of the database
- Calculation of a compound with the help of none linear neuronal network algorithm
- Building of an equation for the simulation of the correlation between factors (compound ingredients) and responses (properties).
Motivation for Program Development

Commerzialisiation of Compound Calculation with neuronal network algorithm

- CAD-CHEM
  - 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

$F_1$ $\rightarrow$ $\rightarrow$ $F_2$ $\rightarrow$ $\rightarrow$ $F_3$

$\Rightarrow$ Objective of the Experiment should be the identification of the most important factors ($F_1,..F_n$), to be able to measure Effects (Responses $R_1,..R_n$) and to describe there dependency in a mathematical equation:

$$R_{i(1...n)} = f(A_0 + A_1F_1 + ....A_nF_n + ....)$$
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

GrafCompounder

- Table calculation software
- Based on Java
- Import / Export function for communication
- Allows automatic mixing of compounds and manual mixing
- Calculates property data
- Shows data composition of the result
- Import / Export of result
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
## Working with the GrafCompounder

- Create a table by copy/paste from Design Expert®
- Assign titles to the rows and columns with:
  - Recipes:
  - Ingredients:
  - Properties:

<table>
<thead>
<tr>
<th>Recipes:</th>
<th>CMPD1</th>
<th>CMPD2</th>
<th>CMPD3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredients:</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
<tr>
<td>Properties:</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
<tr>
<td>Recipes:</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
<tr>
<td>Ingredients:</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
<tr>
<td>Properties:</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
</tr>
</tbody>
</table>
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, Filler 3 and Oil
Comparison
DoE versus GrafCompounder

DoE with 4 Factors
Polymer used was Vistalon 8600

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
<th>Units</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C6630</td>
<td>phr</td>
<td>60.00</td>
<td>95.00</td>
</tr>
<tr>
<td>B</td>
<td>CaCO3</td>
<td>phr</td>
<td>10.00</td>
<td>70.00</td>
</tr>
<tr>
<td>C</td>
<td>Clay</td>
<td>phr</td>
<td>10.00</td>
<td>50.00</td>
</tr>
<tr>
<td>D</td>
<td>Oil</td>
<td>phr</td>
<td>70.00</td>
<td>95.00</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Unit</th>
<th>DoE Optimization</th>
<th>GrafCompounder</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB 6630</td>
<td>phr</td>
<td>73</td>
<td>79</td>
</tr>
<tr>
<td>CaCO3</td>
<td>phr</td>
<td>68</td>
<td>55</td>
</tr>
<tr>
<td>Clay</td>
<td>phr</td>
<td>39</td>
<td>39.5</td>
</tr>
<tr>
<td>Paraffinic Oil</td>
<td>phr</td>
<td>72</td>
<td>73</td>
</tr>
<tr>
<td>MV 120</td>
<td>MU</td>
<td>34</td>
<td>34.9</td>
</tr>
<tr>
<td>T5 (120°C)</td>
<td>min</td>
<td>4.04</td>
<td>4.2</td>
</tr>
<tr>
<td>t10 (170°C)</td>
<td>min</td>
<td>0.45</td>
<td>0.44</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
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<th>Ingredients</th>
<th>Unit</th>
<th>DoE Optimization</th>
<th>GrafCompounder</th>
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<tr>
<td>CB 6630</td>
<td>phr</td>
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<td>73</td>
</tr>
<tr>
<td>CaCO3</td>
<td>phr</td>
<td>68</td>
<td>61</td>
</tr>
<tr>
<td>Clay</td>
<td>phr</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>Paraffinic Oil</td>
<td>phr</td>
<td>72</td>
<td>70</td>
</tr>
<tr>
<td>MV 120</td>
<td>MU</td>
<td>34</td>
<td>34.1</td>
</tr>
<tr>
<td>T5 (120°C)</td>
<td>min</td>
<td>4.04</td>
<td>4.1</td>
</tr>
<tr>
<td>t10 (170°C)</td>
<td>min</td>
<td>0.45</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Optimization area calculated with Design Expert

Solution given by GrafCompounder with the additional condition (CC 6630 – 73 phr)
## Comparison

**DoE versus GrafCompounder**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Unit</th>
<th>DoE Optimization</th>
<th>GrafCompounder</th>
<th>DoE Point Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB 6630</td>
<td>phr</td>
<td>73</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>CaCO3</td>
<td>phr</td>
<td>68</td>
<td>61</td>
<td>61</td>
</tr>
<tr>
<td>Clay</td>
<td>phr</td>
<td>39</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Paraffinic Oil</td>
<td>phr</td>
<td>72</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>MV 120</td>
<td>MU</td>
<td>34</td>
<td>34.1</td>
<td>34.2 ± 3</td>
</tr>
<tr>
<td>T5 (120°C)</td>
<td>min</td>
<td>4.04</td>
<td>4.1</td>
<td>4.01 ± 0.25</td>
</tr>
<tr>
<td>t10 (170°C)</td>
<td>min</td>
<td>0.45</td>
<td>0.45</td>
<td>0.43 ± 0.07</td>
</tr>
</tbody>
</table>
Comparison
DoE versus GrafCompounder

What we have learned

- Calculation with GrafCompounder and optimization result with Design Expert has some characteristic differences
  - GrafCompounder gives always one solution
  - 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 95% confidence interval and measurement error of test methods for the responses.
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

Overlay Plot

Dr. Hans-Joachim Graf
DoE Analysis and Result

Analysis with point prediction results:
- ZF 11.2 MPa
- ZD 335%
- Hardness 66.5°ShA

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ENB</td>
<td>5.58</td>
</tr>
<tr>
<td>B</td>
<td>DTDC</td>
<td>2.11</td>
</tr>
<tr>
<td>C</td>
<td>Sulfur</td>
<td>0.44</td>
</tr>
<tr>
<td>D</td>
<td>MBT</td>
<td>1.00</td>
</tr>
<tr>
<td>E</td>
<td>TiBTD</td>
<td>1.50</td>
</tr>
<tr>
<td>F</td>
<td>ZDiBC</td>
<td>1.50</td>
</tr>
<tr>
<td>G</td>
<td>DTP</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Analysis with GrafCompounder

- Paste table into Graf Compounder
- Select boundaries
Analysis with GrafCompounder

Paste table into GrafCompounder

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

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: ENB</td>
<td>6.5</td>
</tr>
<tr>
<td>B: DTDC</td>
<td>0.98</td>
</tr>
<tr>
<td>C: Sulfur</td>
<td>0.93</td>
</tr>
<tr>
<td>D: MBT</td>
<td>1</td>
</tr>
<tr>
<td>E: TiBTD</td>
<td>1.51</td>
</tr>
<tr>
<td>F: ZDiBC</td>
<td>1.33</td>
</tr>
<tr>
<td>G: DTP</td>
<td>1.45</td>
</tr>
<tr>
<td>ZF</td>
<td>11.5</td>
</tr>
<tr>
<td>ZD</td>
<td>325</td>
</tr>
<tr>
<td>Hardness</td>
<td>67</td>
</tr>
</tbody>
</table>
Run Optimization

Graphical

- Select same boundaries
- ZF-MPa : 11.5-12.0
- ZD-% : 325-335
- H-°ShA : 65-67
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.
## Analysis with GrafCompounder

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

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Result GrafCompounder</th>
<th>Result Design Expert®</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENB</td>
<td>6.5</td>
<td>5.45</td>
</tr>
<tr>
<td>C:Sulfur</td>
<td>0.93</td>
<td>0.88</td>
</tr>
<tr>
<td>B:DTDC</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>D:MBT</td>
<td>1</td>
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<tr>
<td>E:TiBTD</td>
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<td>G:DTP</td>
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<tr>
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<td>330</td>
</tr>
<tr>
<td>Hardness</td>
<td>67</td>
<td>67.5</td>
</tr>
</tbody>
</table>

+) Note: Accelerators are preset!
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