CHBE 552 Project

Comparison of the Simplex Optimization Method with the Gauss-

Newton Method for Parameter Estimation in Algebraic Models

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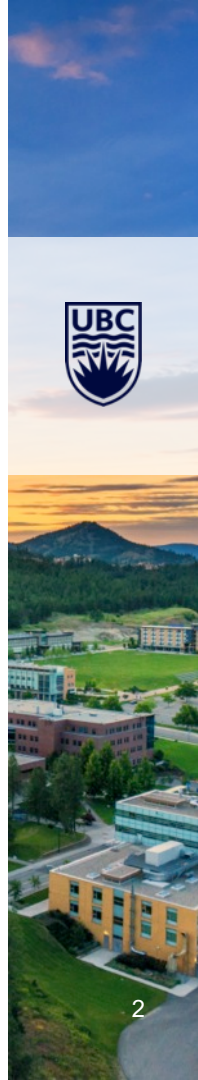
Outline

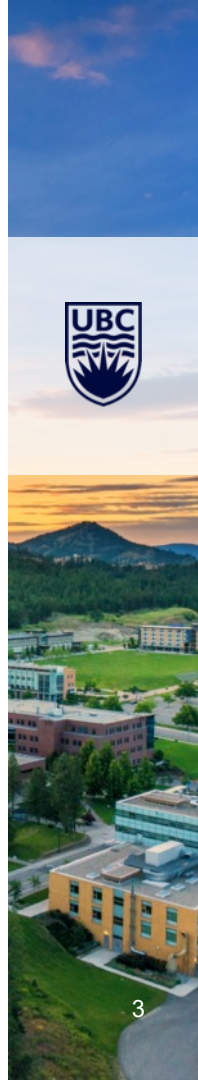
- Gauss-Newton Method with Marquardt's Modification
- Nelder-Mead Algorithm
- Problem 1: Adsorption of 1,2 Dichloropropane
- Problem 2: MnO2-Catalyzed Acetic Acid Oxidation



Gauss-Newton Method with Marquardt's Modification

- Gauss-Newton Method for Non-Linear Least Squares:
  - Aim: Minimize sum of squared differences between observed data and model predictions.
  - Application: Parameter estimation in models linearizable with respect to parameters.
  - Iterative Approach: Refines parameter estimates to reduce discrepancy between observed and predicted values.
  - Update Formula: where J is the Jacobian matrix and r is the residuals vector.

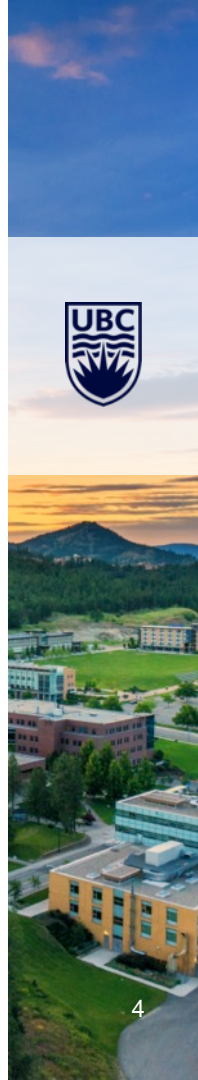
$$\beta_{\text{new}} = \beta_{\text{old}} + (J^T J)^{-1} J^T r$$



Gauss-Newton Method with Marquardt's Modification

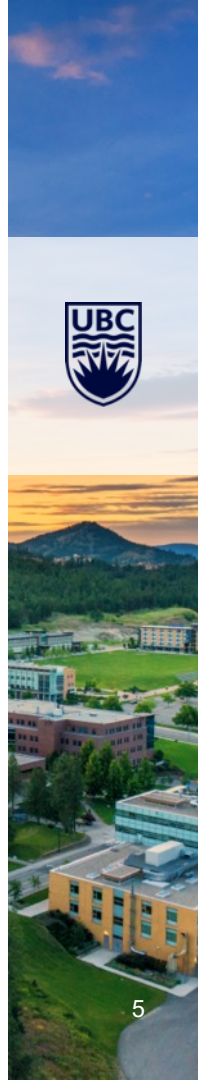
- Marquardt's Modification (Levenberg-Marquardt Algorithm):
  - Enhancement of Gauss-Newton method, introducing a damping factor λ for robustness.
  - Improves convergence, especially when the Jacobian is near singular or not invertible.
  - Combined Approach: Acts like gradient descent with high λ and like Gauss-Newton with low λ.
  - Modified Update Formula: adding flexibility to step size and direction.
  - Goal: Achieve balance between speed (Gauss-Newton) and stability (gradient descent) in parameter estimation.

$$\beta_{\text{new}} = \beta_{\text{old}} + (J^T J + \lambda I)^{-1} J^T r,$$



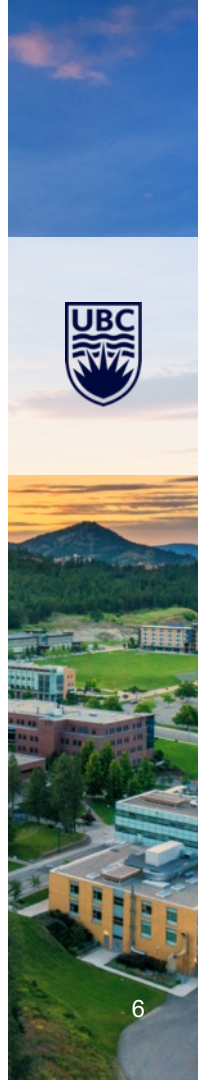
Gauss-Newton Method with Marquardt's Modification

- Computing Confidence Intervals for Parameter Estimates:
  - Covariance Matrix Calculation:
    - Derived from the inverse of the Hessian matrix, approximated by J^T*J, where J is the Jacobian matrix.
    - Use the pseudo-inverse in cases of singularity for stability.
  - Standard Errors of Estimates:
    - Calculated as the square root of the diagonal elements of the covariance matrix.
  - Confidence Interval Calculation:
    - Confidence intervals are determined using the standard errors, a critical value from the t-distribution, and the degrees of freedom.
    - Formula: Estimate ± (t-critical × Standard Error)



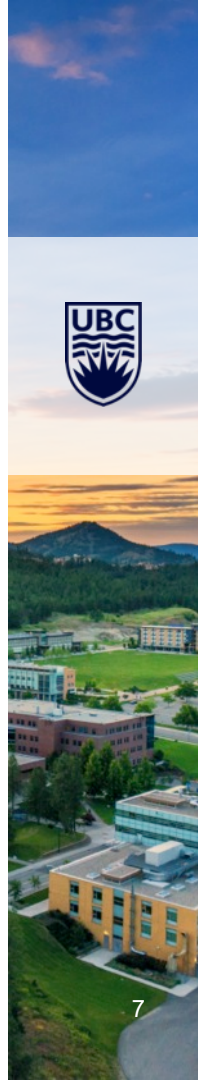
Nelder-Mead Algorithm

- Direct search method for minimizing an objective function.
- Suitable for non-linear, non-smooth functions without requiring derivatives.
- Operates using a simplex (a polytope in higher dimensions) to represent candidate solutions.



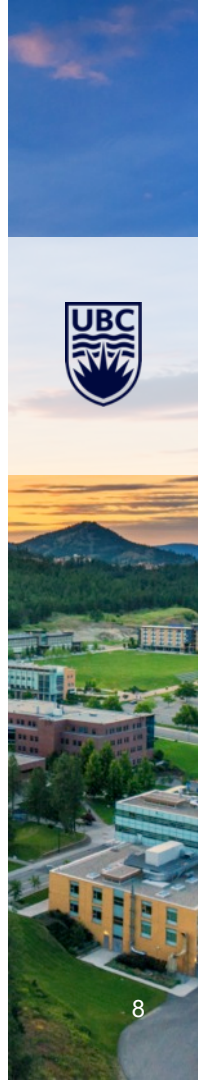
Nelder-Mead Algorithm

- Key Steps of the Nelder-Mead Method:
  - Initialization: Generate an initial simplex around a starting point.
  - Evaluation: Calculate the objective function at each simplex vertex.
  - Transformation: Perform operations to update the simplex:
  - Reflection: Reflect the worst point across the centroid if it improves.
  - Expansion: Take a larger step if reflection finds a new best point.
  - Contraction: Move the worst point closer to the centroid if reflection fails.
  - Shrinkage: Reduce the simplex size around the best point for finer exploration.
  - Termination: Repeat until reaching a stop condition (e.g., minimal objective function change, small simplex, maximum iterations).



Nelder-Mead Algorithm

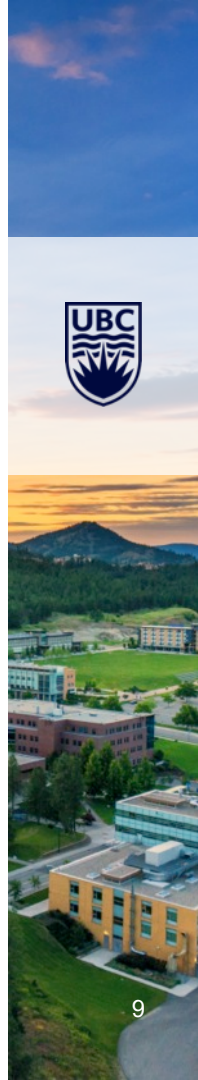
- Advantages: Simple implementation, no need for derivative information, versatile across complex functions.
- Limitations: Potential for slow convergence or convergence to non-optimal points, especially in rugged landscapes or high dimensions.
- Applications: Ideal for parameter estimation in models where gradient-based methods are inapplicable due to lack of derivatives or presence of many local minima.



Problem 1: Adsorption of 1,2 Dichloropropane

- **Determine the parameters (q_{sat}, k, t) of the adsorption model (equation 1) of [1]**
  - $$q = q_{sat} * \frac{k * p}{[1 + (k * p)^{t}]^{\frac{1}{t}}}$$

    - q : amount adsorbed
    - q_{sat} : saturation amount adsorbed
    - k : equilibrium constant
    - p : pressure
    - t : parameter that characterizes the system heterogeneity
- **Determine the 95 % confidence interval of the parameters**

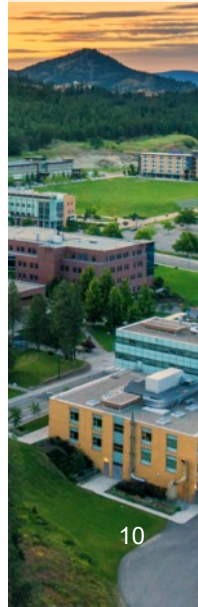


Problem 1: Adsorption of 1,2 Dichloropropane

Table 2. Experimental Isotherm Data for 1,2-Dichloropropane on Activated Carbon

p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}	p/kPa	q/mol kg^{-1}
$T = 303$ K		$T = 338$ K		$T = 373$ K		$T = 423$ K		$T = 473$ K	
0.3427	1.9267	0.3559	1.2594	0.3651	0.5874	0.3849	0.3102	0.3981	0.1175
0.5134	2.1711	0.5332	1.4662	0.5470	0.7237	0.5766	0.3853	0.5964	0.1551
0.6837	2.3449	0.7100	1.6353	0.7284	0.8365	0.7678	0.4525	0.7941	0.1833
0.8535	2.4530	0.8863	1.7556	0.9093	0.9305	0.9586	0.4944	0.9914	0.2054
1.0229	2.5799	1.0622	1.8581	1.0898	0.9803	1.1488	0.5503	1.1881	0.2162
1.1918	2.6612	1.2377	1.9577	1.2697	1.0818	1.3385	0.5954	1.3843	0.2547
1.5284	2.7937	1.4126	2.0324	1.4493	1.1316	1.5277	0.6297	1.5801	0.2693
1.7821	2.8510	1.5872	2.1109	1.6283	1.2030	1.7165	0.6767	1.7753	0.2923
2.1239	2.9159	1.8313	2.2044	1.8663	1.2768	1.9576	0.7265	2.0347	0.3163
2.5752	2.9991	2.1936	2.3167	2.2458	1.3440	2.3329	0.7810	2.4199	0.3407
3.2134	3.1062	2.7723	2.4243	2.8411	1.4685	2.9556	0.8623	3.0243	0.3839
3.5572	3.1438	3.2543	2.4803	3.2951	1.5268	3.4313	0.9253	3.5130	0.4145
3.6790	3.1551	3.6185	2.5766	3.6798	1.6034	3.8025	0.9662	3.8945	0.4370
4.3900	3.2730	3.7590	2.6024	3.8230	1.6198	3.9350	0.9826	4.0469	0.4474
4.8735	3.3012	4.5065	2.7204	4.6036	1.7199	4.7008	1.0526	4.7785	0.4737
5.1615	3.3228	5.0040	2.7979	5.0910	1.7857	5.2216	1.0982	5.2651	0.5066
		5.2772	2.8130	5.3930	1.8120	5.5087	1.1194	5.5550	0.5202

Figure 1: Raw Data for Problem [1]



Problem 1: Adsorption of 1,2 Dichloropropane

- Result
  - By GN-M:

T	q_sat	k	t
303	4.31 ± 0.19	17.73 ± 5.73	0.46 ± 0.05
338	5.2 ± 0.56	7.99 ± 2.6	0.37 ± 0.05
373	4.56 ± 1.09	1.72 ± 0.41	0.38 ± 0.07
423	6.77 ± 6.75	0.8 ± 0.23	0.28 ± 0.13
473	4.41 ± 12.2	0.27 ± 0.17	0.3 ± 0.32

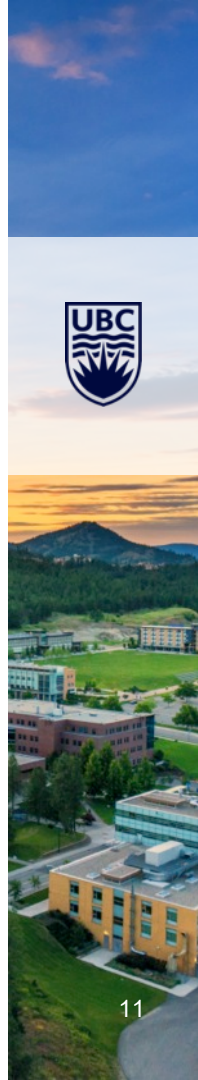
  - By NMA:

T	q_sat	k	t	CI for q_sat	Ci for k	CI for t
303	4.31	17.81	0.45	[4.25 4.47]	[16.21 20.28]	[0.43 0.47]
338	5.58	9.99	0.34	[5.21 5.29]	[7.82 9.2]	[0.36 0.36]
373	5.68	2.1	0.33	[5.65 5.68]	[1.98 2.21]	[0.32 0.33]
423	5.77	0.74	0.31	[5.38 5.85]	[0.73 0.78]	[0.3 0.31]
473	2.92	0.3	0.35	[2.82 2.99]	[0.26 0.32]	[0.34 0.37]

- Validation

Table 3. Fitted Values and Standard Deviations of Adsorption Equilibrium Constants (Eq 1) and the Estimated Values of the Henry Law Constant (Eq 2)

T / K	q_{sat} / mol kg^{-1}	k / kPa^{-1}	t	$\sigma_{model}{}^{a}$ / mol kg^{-1}	K_H / mol kg^{-1} kPa^{-1}
303	4.31 ± 0.15	17.7 ± 4.7	0.46 ± 0.04	0.02	146
338	5.20 ± 0.45	7.99 ± 2.08	0.37 ± 0.04	0.02	17.0
373	4.56 ± 0.58	1.72 ± 0.22	0.38 ± 0.04	0.01	3.31
423	5.65 ± 1.15	0.76 ± 0.05	0.31 ± 0.03	0.01	1.21
473	3.24 ± 1.69	0.29 ± 0.04	0.34 ± 0.08	0.01	0.37



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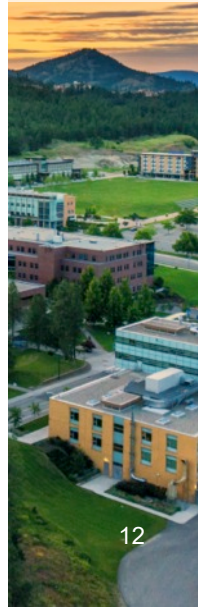
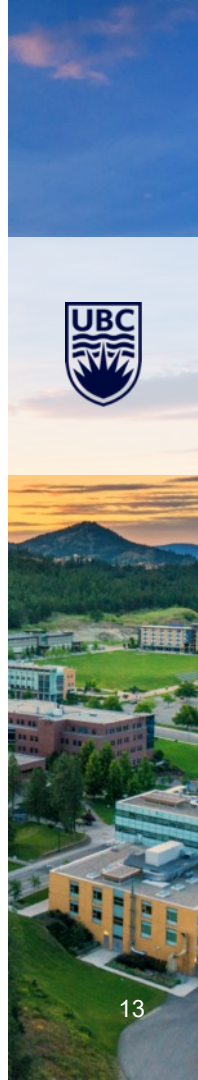


Problem 2: MnO2-Catalyzed Acetic Acid Oxidation

- **Determine the parameters (k_1, k_2, k_3) in equation (3) of [2]**
- **Object equation**

$$W/F_{A0} = \frac{(1 + k_3[O_2]_0)^2\{k_2[HOAc]_0 X - \ln(1 - X)\}}{k_1[HOAc]_0[O_2]_0} \quad (3)$$

  - X is the conversion of acetic acid
  - $\frac{W}{F_{A0}}$ is the catalyst mass/acetic acid molar flow rate into the reactor ratio
- **Determine the 95 % confidence interval of the parameters**



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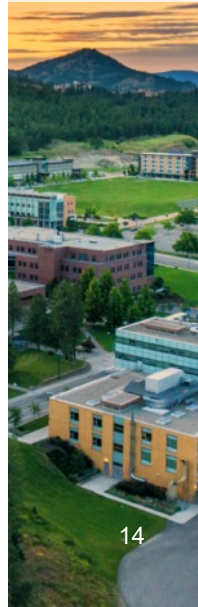

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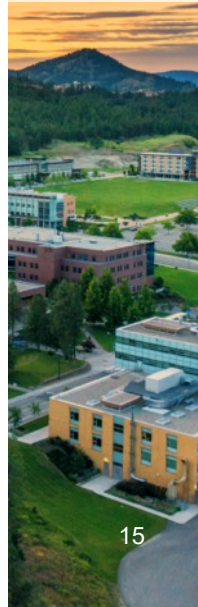

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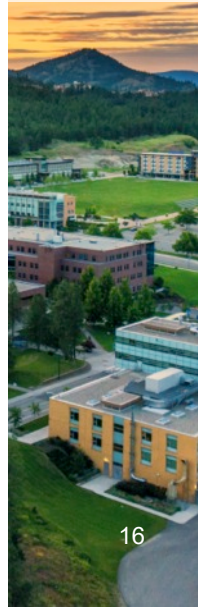

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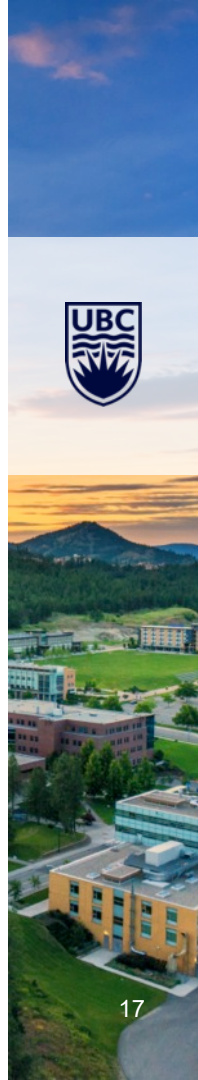


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