# Validation of Supercritical Fluid Extraction Model Through COMSOL Multiphysics 5.2

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**Abstract:** In this work, mathematical model of supercritical fluid extraction process given by Sovova H., 1994 has been solved by COMSOL Multiphysics 5.2 tool. Sovova et al., 1994 used this model for the supercritical $CO_2$ extraction of grape seed. Extraction was performed at 40 $^0$C and 280 bar with different specific flow rates and grade of grinding. Further Mira et al., 1996 and Mira et al., 1999 validated the same model for the supercritical $CO_2$ extraction of orange peel. These results are plotted on COMSOL Multiphysics 5.2 tool and compared with the results obtained by Sovova and Mira which gives the successful fit of this mathematical model on the software. A very small average absolute relative deviation (AARD) has been observed between the results of COMSOL Multiphysics and the results given in literature.

**Keywords:** SFE, Extraction, Zones, Modeling, Grape seed, Orange peel, AARD

## 1. Introduction

In the age of development, there could be many reasons that can cause the negative effect on the environment, so the focus of modern research is towards the 'Green' process. Supercritical fluid extraction (SFE) is such type of innovative approach in the separation techniques. This process separates the product at supercritical temperature and pressure condition of solvent.

The most interesting properties of supercritical fluid are liquid like density and gas like viscosity. Diffusivity of supercritical fluid is intermediate between gas and liquid. These properties help to increase the solvent capacity of supercritical fluid to extract more. To describe this process, many mathematical models have been used in the past. Out of which, Sovova H., 1994 is one of the best mathematical models describing the extraction from almost all parts of the plant. This model was based on the concept of broken and intact cell (BIC) model. Sovova et al., 1994 used this model for the extraction of grape seed. Further Mira et al., 1996 and Mira et al., 1999 validated this model for the extraction of orange peel. The purpose of present work is to simulate the Sovova's model in COMSOL Multiphysics 5.2 tool and validate the model.

## 2. Mathematical Modeling

Sovova H., 1994 developed a mass transfer based mathematical model based on broken and intact (BIC) phenomenon. He defined the total extraction curve into three zones as shown in figure 1. First zone is fast extraction zone which is due to the extraction of easily accessible oil from broken part of seed. Easily accessibly oil is that part of oil that occurs on surface of particle due to grinding and milling. Second zone is transition zone which is the combination of extraction of easily accessible oil and inaccessible oil. In this zone, it is observed that along with the accessible oil, the inaccessible oil also starts pouring out. Third extraction zone represents slow extraction which describes the extraction of inaccessible oil from intact part of seed.

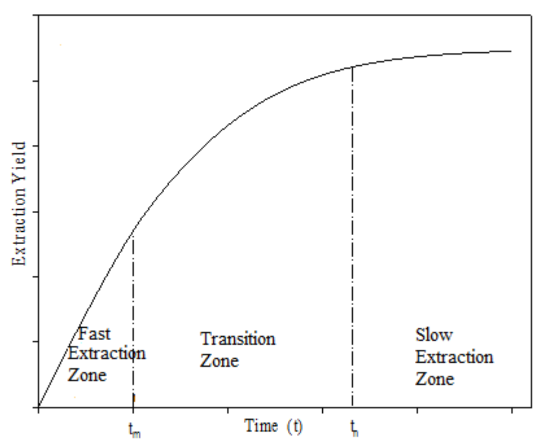



**Figure 1: Zones of extraction curve**

### 2.1 Partial differential equations

A mass balance approach has been applied across the extraction bed for the solid phase and solvent phase with respect to bed height (*H*) and extraction time (*t*).

For solid phase:

$$-\rho_s(1-\varepsilon)\frac{\partial x}{\partial t}=J(x,y) \qquad \textbf{.......(1)}$$

For solvent phase:

$$\rho U\frac{\partial y}{\partial h}=J(x,y) \qquad \textbf{.......(2)}$$

Here, $J\ (x,y)$ is mass transfer rate of solute in solid and solvent phase. $\rho$ and $\rho_s$ are density of solvent and solid respectively. $\varepsilon$ is the void fraction of packed bed. $U$ is the superficial velocity of solvent. $x$ and $y$ are the solute concentration in solid and solvent phase respectively.

$x_k$ is the fraction of easily accessible oil. Rate of mass transfer will be higher in the particle having concentration greater than $x_k$.

$$J(x>x_k,y)>J(x\le x_k,y) \qquad \textbf{......(3)}$$

Mass transfer rates for solvent and solid phase are as follows:

$$J(x>x_k,y)=k_f a_0\rho(y_r-y) \qquad \textbf{...(4)}$$

$$J(x\le x_k,y)=k_f a_0\rho(y_r-y)\,{}^{x}\!/\!_{x_k} \qquad \textbf{.....(5)}$$

### 2.2 Boundary conditions & Initial conditions

$x_0$ is the initial concentration (kg) of solute in the solid phase (kg). At the entrance of extractor, there is solute in solvent phase.

$$x(h,t=0)=x_0$$
$$y(h=0,t)=0. \qquad \textbf{........(6)}$$

### 2.3 Analytical equations

Extraction rate is determined as:

$$e(t)=e\left(q-\dot{q}\,t\right)=x_0-\left({}^{1}\!/\!_{H}\right)\int_0^H x(h,t)\,\mathrm{d}h. \qquad \textbf{......(7)}$$

After solving equations 1, 2, 4, 5 and 7 with initial and boundary condition, extraction curve for all three zones are determined as:

$$e=\begin{cases} q\,y_r[1-\exp(-Z)] & \text{for } q<q_m \\ y_r[q-q_m\exp(z_w-Z)] & \text{for } q_m\le q<q_n \\ x_0-\dfrac{y_r}{W}\ln\left\{1+\left[\exp\left({}^{Wx_0}\!/\!_{y_r}\right)-1\right]\exp[W(q_m-q)]\,{}^{x_k}\!/\!_{x_0}\right\} & \text{for } q\ge q_n \end{cases}$$

Where,

$$q_m={}^{(x_0-x_k)}\!/\!_{y_r Z}$$

$$q_n=q_m+\frac{1}{W}\ln\frac{x_k+(x_0-x_k)\exp\left({}^{Wx_0}\!/\!_{y_r}\right)}{x_0}$$

$$\frac{z_w}{Z}=\frac{y_r}{Wx_0}\ln\frac{x_0\exp[W(q-q_m)]-x_k}{x_0-x_k}$$

$$Z=\frac{k_f a_0\rho}{[\dot{q}(1-\varepsilon)\rho_s]}=\frac{F}{\dot{q}}$$

$$W=\frac{k_s a_0}{[\dot{q}(1-\varepsilon)]}=\frac{S}{\dot{q}}$$

$q_m$ and $q_n$ are the amount of $CO_2$ used in fast extraction zone and transition zone respectively. $z_w$ is the intermediate boundary between the fast and slow extraction zone. Parameters $Z$ and $W$ are related to solvent phase mass transfer coefficient ($k_f$) and solid phase mass transfer coefficient ($k_s$). Solubility is defined as $y_r$ and specific solvent flow rate is defined as $\dot{q}$.

## 3. Model Solved by Using COMSOL Multiphysics 5.2

To solve these three analytical equations in COMSOL Multiphysics 5.2 tool, following steps has been taken:

COMSOL multiphysics --> Model Wizard --> Select 1 D space dimension --> No physics selected --> Click done

COMSOL multiphysics --> Definitions tool bar --> Analytic function (three times for three analytical functions) (Appendix A1)

There is one more alternative to define Analytic functions.
COMSOL multiphysics --> Component 1 --> Definitions (Right click) --> Functions --> Analytics (Appendix A2)

Define Parameter for the functions;
COMSOL multiphysics --> Global --> Definitions (Right click) --> Parameter
Define Parameter in setting window of Parameter (Appendix A3).

Define analytic functions, arguments and conditions in the setting window of Analytic;
Analytic --> Definition --> Expression and Arguments
Analytic --> Plot Parameter --> Upper and Lower limit --> Create Plot (Appendix A4)

Define Parameter Bounds
COMSOL multiphysics --> Results --> Data Sets --> Function 1D --> Parameter Bounds (Appendix A5)

COMSOL multiphysics --> Results --> 1 D Plot Group (Right click) --> Line Graph --> Data (in setting window of Line Graph) --> Data set (Define function 1D) (Appendix A6)

Define y-Axis data and x-Axis data in the setting window of Line Graph to get the desired graph and plot the results.
Repeat the above procedure for all three analytic functions and add more Line graphs to plot all three equations together.

## 4. Results & Discussion

This section analyzed and discussed the results of Sovova's model given in research papers (Sovova et al., 1994; Mira et al., 1996 and Mira et al., 1999) and the results are than compared with the results obtained from COMSOL Multiphysics 5.2 tool. Analysis of the results is presented with the calculation of AARD. Experimental data of these papers are given in table 1.

### 4.1 Sovova et al., 1994

Sovova et al., 1994 performed a supercritical fluid extraction of grape seed at temperature 40 $^{0}$C and pressure 280 bar. In his study, he investigated the effects of milling and specific solvent flow rate on the extraction yield. He plotted the result between dimensionless amounts of extract 'e' (kg extract/kg seed) and dimensionless amount of solvent 'q' (kg solvent/kg seed). Figure 2 was plotted at different specific flow rate. The graph shows that the amount of extract is almost constant (0.125 kg oil/kg seed) and gives almost similar graph except at the transition zone. It means that as the flow rate increases, transition zone is transferring from sharp turn to smooth curve.

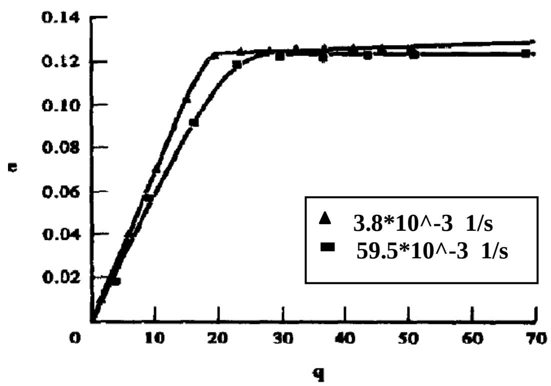



**Figure 2: Effect of specific solvent flow rate, given by Sovova et al., 1994**

Figure 3 is the result obtained from COMSOL Multiphysics 5.2 tool with the same operating

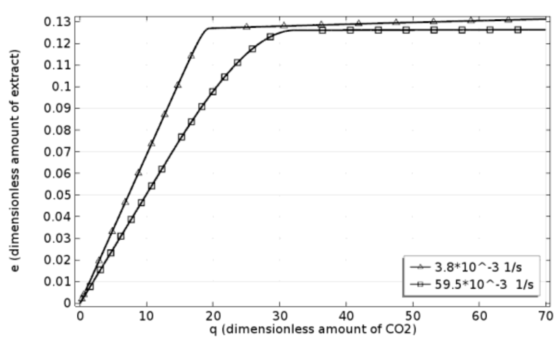



**Figure 3: Effect of specific solvent flow rate, given by COMSOL Multiphysics 5.2**

**Table 1: Experimental data of Sovova et al., 1994; Mira et al., 1996 and Mira et al., 1999**

| Name | Sovova et al., 1994 | | Mira et al., 1996 | | Mira et al., 1999 | | Description |
|---|---|---|---|---|---|---|---|
| $x_0$ | 0.144 | | 0.1 | | 0.045 | | Initial oil content of seed |
| $x_k$ | 0.018 | | 0.06 | | 0.012 | | Initial oil concentration inside the particles |
| $U$ | $3.3\times10^{-4}$ | | | | | | Superficial velocity of solvent, m/s |
| $S$ | $2.2\times10^{-5}$ | | | | | | Parameter for W, $s^{-1}$ |
| $F$ | $6.0\times U^{0.54}$ | 0.079095 | | | | | Parameter for Z, $s^{-1}$ |
| $k_f$ | $2.2\times10^{-4}\times U^{0.54}$ | $2.9001\times10^{-6}$ | $1.13\times10^{-4}$ | | $1.13\times10^{-4}$ | | Mass transfer coefficient for fluid phase, m/s |
| $k_s$ | $6.6\times10^{-10}$ | | $2.26\times10^{-5}$ | | $2.26\times10^{-5}$ | | Mass transfer coefficient for solid phase, m/s |
| $y_r$ | 0.00685 | | 0.095 | | 0.008 | | Solubility |
| $Z\times\dot{q}$ | | | $1.13\times10^{-4}$ | | $1.52\times10^{-3}$ | | Variable for Z |
| $W\times\dot{q}$ | | | $2.26\times10^{-5}$ | | $1.273\times10^{-4}$ | | Variable for W |
| $\rho$ | 899 | | | | | | Density of solvent, $kg/m^3$ |
| $\rho_s$ | 1089.5522 | | | | | | Density of solid, $kg/m^3$ |
| $\varepsilon$ | 0.33 | | 0.33 | | 0.33 | | Void fraction of bed |
| $\dot{q}$ | $3.8\times10^{-3}$ | | $1.26\times10^{-3}$ | | 1.29 | | Specific flow rate of solvent, $s^{-1}$ |
| $Z$ | $F/\dot{q}$ | 20.814 | $(Z\times\dot{q})/\dot{q}$ | 0.089683 | $(Z\times\dot{q})/\dot{q}$ | 0.001178 | Parameter |
| $W$ | $S/\dot{q}$ | 0.0057895 | $(W\times\dot{q})/\dot{q}$ | 0.017937 | $(W\times\dot{q})/\dot{q}$ | 0.10804 | Parameter |

conditions. Comparative study shows a good match between these results with a very small AARD of 2.940 %.

AARD is calculated as:

$$AARD = \frac{1}{n}\sum\frac{(MV - OV)\times 100}{OV}$$

MV: Model value
OV: Original value
n: No. of data point

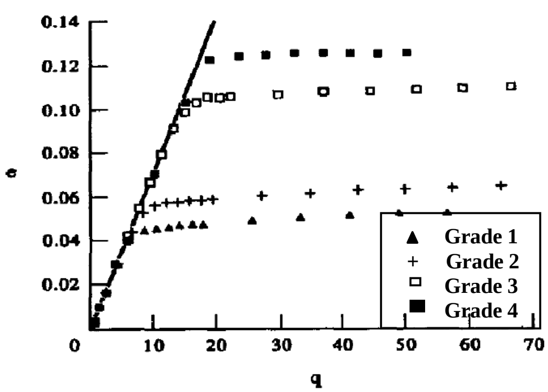



**Figure 4: Effect of Grade of grinding, given by Sovova et al., 1994**

Figure 4 shows the effects of Grade of Grinding (sieve range 0.08 – 1 mm) on extracted amount of solute, given by Sovova et al., 1994. Grade 1 represents the more number of large particles and Grade 4 represents more number of small particles

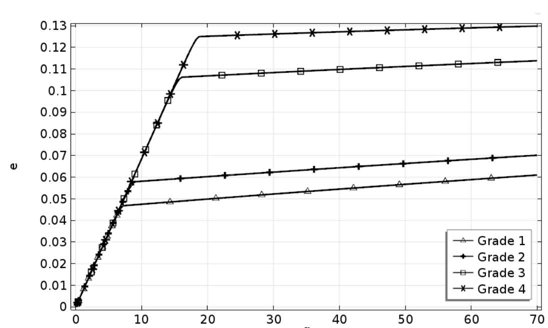



**Figure 5: Effect of Grade of grinding, given by COMSOL Multiphysics 5.2**

Figure 5 is the graph of Grape seed extraction, plotted with COMSOL Multiphysics 5.2. COMSOL is giving a good representation of the original result with AARD in the range of 0.895-4.309 %. Error band for extraction of Grape seed is ± 9.26%.

### 4.2 Mira et al., 1996

Mira validated Sovova's model in the supercritical $CO_2$ extraction of essential oil from orange peel at pressure of 150 bar and temperature of 50 $^0$C. Particle size used for the extraction is 0.3 mm. In his study, he investigated the effect of solvent flow rate on the mass extracted with respect to solvent ratio as shown in figure 6. It can be seen from the graph that, initially, there is not much difference in the extraction till 2.5 kg/h. After this flow rate, a small change occurred, showing the effect of flow rate. The results were plotted on the SOLVER function of EXCEL 5.0 spreadsheet.

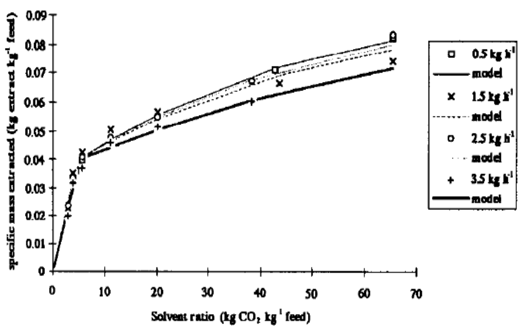



**Figure 6: Effect of solvent flow rate, given by Mira et al., 1996**

Figure 7 is the result plotted with COMSOL Multiphysics 5.2 which is compared with the result obtained by solver function of EXCEL.

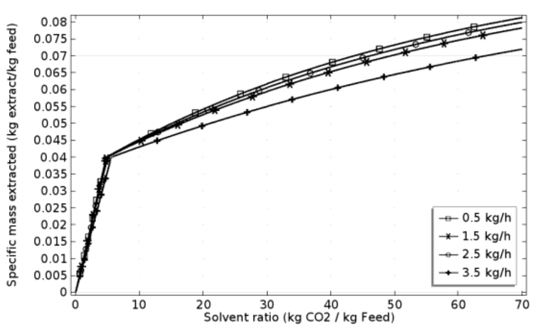



**Figure 7: Effect of solvent flow rate, given by COMSOL Multiphysics 5.2**

Comparison reflects a good fitting of COMSOL tool with the result obtained in literature and successfully validates Sovova's model in COMSOL. A very small value of AARD is determined for these plots are in range of 0.2415-2.499 %.

### 4.3 Mira et al., 1999

In 1999, Mira validated Sovova's model for the extraction of cuticular waxes from orange peel. He investigated the effect of solvent flow rate on the mass extracted 'e' with respect to solvent ratio 'q'. The operating condition was same as Mira et al., 1996 with one difference of mass transfer mechanics. Mass transfer mechanism is different for cuticular waxes and essential oil. SOLVER function of EXCEL 5.0 spreadsheet was used to plot the result (figure 8).

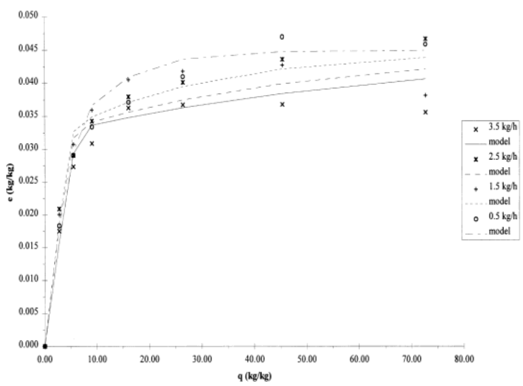



**Figure 8: Effect of solvent flow rate, given by Mira et al., 1999**

In figure 9, same operating condition is plotted on COMSOL Multiphysics 5.2 tool which gives a very good fitting of Sovova's model.

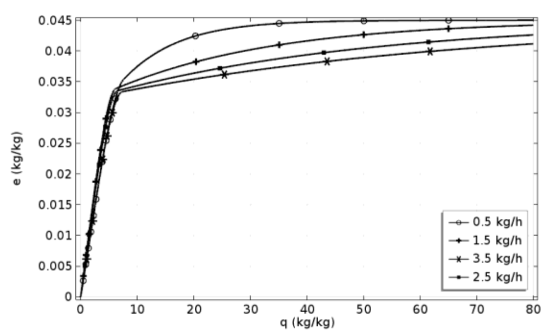



**Figure 9: Effect of solvent flow rate, given by COMSOL Multiphysics 5.2**

The smallest value of AARD is observed for the model is within the range of 0-1.046 %. Range of error band for orange peel is ± 4.44%.

Except this, one more advantage of this software is its computation time. It took approximately 10-15 seconds to compute these plots individually which is very less time as compared to other software.

## 5. Conclusions

On the basis of the existing literature and the results of the proposed study it can be concluded that COMSOL Multiphysics 5.2 is an appropriate tool for Sovova H., 1994 model. Further the results show a negligible value of AARD within ± 9.26% error band for grape seed and ± 4.44% error band for orange peel which makes the software a reliable tool for modeling and validation of model equations.

Thus COMSOL multiphysics 5.2 can be seen as one of the most reliable modeling software in supercritical fluid extraction technique because of its less computation time, comfort handling and better results.

## 6. References


1. Sovova H., Rate of the vegetable oil extraction with supercritical $CO_2$-I modeling of extraction curves, Chemical Engineering Science, 49: 409-414, (1994).

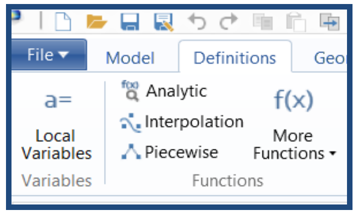
2. Sovova H., Kucera J., Jez J., Rate of the vegetable oil extraction with supercritical $CO_2$–II extraction of grape oil, Chemical Engineering Science, 49: 415-420, (1994).

3. Mira B., Blasco M., Subirates S., Supercritical $CO_2$ Extraction of Essential Oils from Orange Peel, The Journal of Supercritical Fluids, 9, 238-243, (1996).

4. Mira B., Blasco M., Berna A., Subirates S., Supercritical CO2 extraction of essential oil from orange peel. Effect of operation conditions on the extract composition, Journal of Supercritical Fluids, 14, 95–104 (1999).


## 7. Appendix

**A1:**

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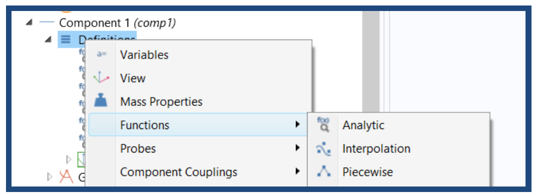



**A3:**

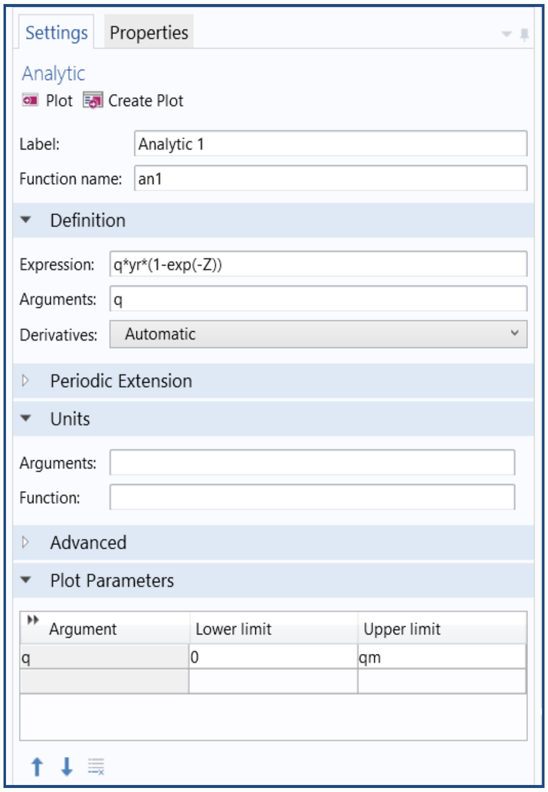
Settings | Properties

Parameters

▾ Parameters

| Name | Expression | Value | Description |
|---|---|---|---|
| x0 | 0.144 | 0.144 | Initial oil content of seed |
| xk | 0.018 | 0.018 | Initial oil concentration in... |
| U | 3.3*10^-4 | 3.3000E-4 | Superficial velocity of solv... |
| F | 6.0*U^(0.54) | 0.079095 | Parameter for Z |
| S | 2.2*10^-5 | 2.2000E-5 | Parameter for W |
| kf | 2.2*10^(-4)*U^0.54 | 2.9001E-6 | Mass transfer coefficient f... |
| ks | 6.6*10^(-10) | 6.6000E-10 | Mass transfer coefficient f... |
| yr | 0.00685 | 0.00685 | Solubility |
| rho | 899 | 899 | Density of solvent |
| rhos | 1089.5522 | 1089.6 | Density of solid |
| ep | 0.33 | 0.33 | Void fraction of bed |
| q_dot | 3.8*10^-3 | 0.0038 | Specific flow rate of solvent |
| Z | F/(q_dot) | 20.814 | Parameter |
| W | S/(q_dot) | 0.0057895 | Parameter |
| qm | (x0-xk)/(yr*Z) | 0.88372 | Amount of CO2 used in fa... |
| qn | qm+(1/W)*log((xk+(x... | 19.414 | Amount of CO2 used in tr... |

**A4:**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Upper limit
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0
qm

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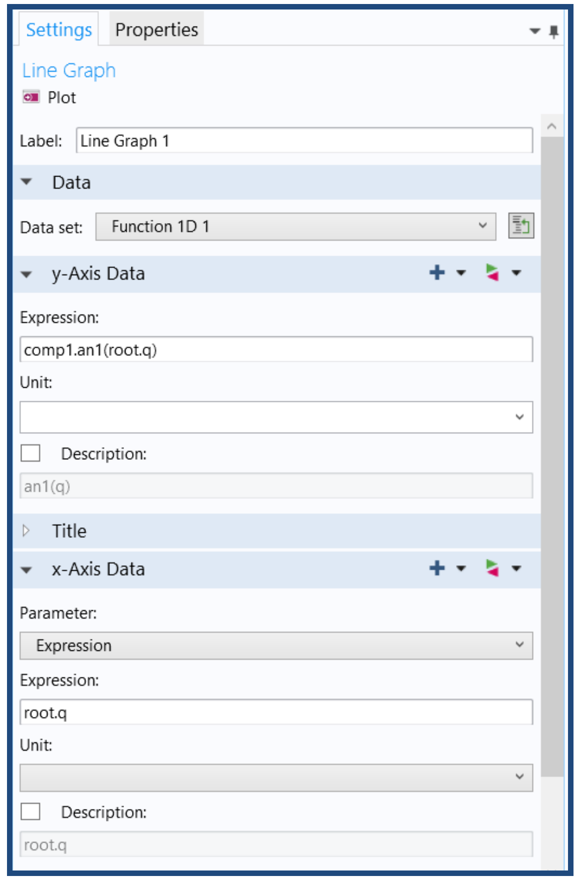
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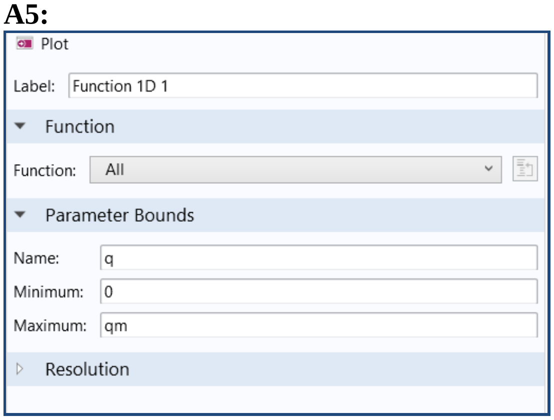
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qm
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