CCSI Basic Data Fitting Tools

SorbentFit User Manual

Version 2.0.0

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Table of Contents

List of Tables

To obtain support for the products within this package, please send an e-mail to ccsi-support@acceleratecarboncapture.org.

CCSI Basic Data Fitting Tools

1.0 ABSTRACT

Sorbentfit is a suite of routines that fit combined thermodynamic and kinetic models of amine-based CO_2 solid sorbents to laboratory and bench-scale data. There are two levels of models included with the code: a lumped kinetic model and a reaction-diffusion model with zwitterion chemistry. The lumped kinetic model is faster, while the reaction-diffusion model is more accurate. Both models can be fit to thermogravimetry and fixed-bed data. Fits can be either point estimates of parameters, achieved using a particle swarm optimizer, or Bayesian calibration, which results in a distribution of parameter values. *Sorbentfit* does not require any third-party software; it runs in Windows®, Mac®, and UNIX®/Linux™ operating systems.

2.0 REPORTING ISSUES

To report an issue, please send an e-mail to ccsi-support@acceleratecarboncapture.org.

3.0 VERSION LOG

Product	Version Number	Release Date	Description
SorbentFit	**2.0.0**	**3/31/2018**	**Initial Open Source release**
CCSI Basic Data Fitting Tools	**2015.10.00**	**11/15/2015**	**2015 November IAB Release**
Sorbentfit	2015.10.0	10/31/2015	2015 October IAB Release – In addition to previous features, a new feature has been added to the OpenMP and Windows package. Now Bayesian Analysis is included for TGA. Also a parametric study routine has been added as well.
Sorbentfit	2015.06.0	06/30/2015	2015 July Release – The source code now creates an output file for the iteration data that matches the timestamp on the data. Also created are copies of the filelist and configuration files that were used in the simulation, these also carry the unique timestamp. *Sorbentfit* now calculates the program run time.
Sorbentfit	2014.10.0	10/31/2014	2014 October IAB Release – The empfit_humid now estimates any combination of parameters on the MPI and OMP versions. A version for Windows®, which partially supports the above functionality, has also been added.

Sorbentfit (TGA)

1.0 INTRODUCTION

This package contains tools for conducting empirical fitting, Bayesian Analysis, and parametric studying for the Carbon Capture Simulation Initiative (CCSI) first-generation sorbent kinetic model. The fitting routine uses a Particle Swarm Optimizer (PSO) to fit the model to Thermo Gravimetric Analysis (TGA) data. The output of the routine is a set of model parameters corresponding to the CCSI first-generation sorbent model, which represent a best fit (in a least-squares sense) of the model to the data provided. The routine should be appropriate for any amine-based solid sorbent. The Bayesian Analysis (**OpenMP only**) uses a Markov Chain Monte Carlo (MCMC) routine to provide a posterior distribution of parameters, along with quantification of uncertainty.

Additionally, the package provides the capability of evaluating the first-generation model for an arbitrary sets of parameters and an arbitrary profile of temperatures and gas compositions.

2.0 THEORY AND USE

2.1 Model Overview

The CCSI first-generation sorbent model is written:

$$\frac{\partial x}{\partial t} = k_c[s^2 p_c - xw/\kappa_c]$$

$$\frac{\partial a}{\partial t} = k_h[p_h - a/\kappa_h] - k_b[sap_c - bw/\kappa_b]$$

$$\frac{\partial b}{\partial t} = k_b[sap_c - bw/\kappa_b]$$

$$s = 1 - x - w$$

$$w = x + b/n_v$$

$$\kappa_z = \exp\left(\frac{\Delta S_z}{R}\right)\exp\left(\frac{-\Delta H_z}{RT}\right)/P$$

$$k_z = \zeta_z \exp\left(\frac{-\Delta H_z^{\ddagger}}{RT}\right)$$

where:

Table 1: Equation Parameters

Variable	Description
x	Carbamate Site Fraction
b	Bicarbonate Concentration
a	Adsorbed Water Concentration
w	Protonated Amine Site Fraction
s	Free Amine Site Fraction
p_c	CO_2 Partial Pressure
p_h	H_2O Partial Pressure
P	Total Pressure
n_v	Number of Amine Sites per Unit Volume
ΔH_z	Formation Enthalpy of Species z
$\Delta H^{\neq}_z$	Activation Energy for Reaction z
ΔS_z	Formation Entropy of Species z
ζ_z	Pre-Exponential Factor for Reaction z

The model considers the chemisorption of CO_2 to form carbamate, the physisorption of water, and the formation of bicarbonate from a gaseous CO_2 molecule and adsorbed water, assuming that the kinetics of each are dominated by a single, ideally-behaved chemical reaction. There are a total of 13 parameters estimated: the entropy and enthalpy of formation for each species (carbamate, physisorbed water, and bicarbonate), the activation energy and pre-exponential factor for each reaction, and the number of active adsorption sites per unit volume.

2.2 Usage

The model parameters can be estimated in two ways. First the parameters can be estimated by fitting the model to experimental data. Secondly, the parameters can be estimated through Bayesian Analysis. This is the purpose of *Sorbentfit*. *Sorbentfit* estimates the parameters for CO_2-only, H_2O-only, and CO_2-H_2O mixture cases (including n_v). Value ranges for the parameters are supplied in the configuration files described below.

Units

All units should be SI.

TGA Data Files and Filelist

The packages depend on TGA data files located in the subfolder “data.” The files pertaining to each type of run (dry CO_2, water-only, and wet CO_2) are listed in text files located in the filelist folder for the OpenMP and MPI-based packages and the top directory of the package for the Windows package. For the OpenMP and MPI versions, the file is named “filelist.txt.” In the “filelist” file, the first two lines must contain the total number of filenames listed in the file, followed by the numbers “4” & “1” on the next line, then each filename listed on a separate line, with the string “data/” prepended. For example, a file named “TGA1.txt” would be listed “data/TGA1.txt.”

In the data files, the first line must contain a single number specifying the total number of data lines to follow. Each following line contains the information, which is delimited by spaces:

CO_2 Pressure (Pa) | H_2O Pressure (Pa) | Temperature (K) | Time (s) | Experimental Weight Fraction

The time of the first full line need not be zero, but it is assumed that the sorbent was purged of all CO_2 and water at time t = 0.

The default data files contained in the folder "data" and listed in the "filelist" file are the actual experimental data for the CCSI sorbent of focus, NETL-32D.

Particle Swarm Optimizer (PSO)

The first way to estimate the parameters is to use the Particle Swarm Optimizer (PSO).

Configuration File

The configuration file is an important file located in the main folder. This file contains all 13 parameters that *Sorbentfit* can use for parameter optimization and simulation of dry, water, and humid cases. This file contains settings for the ODE solver (which may be left in their default configuration) such as the time step and convergence tolerances, followed by the total pressure in the TGA chamber and the sorbent density. The lines to follow differ depending on the case (dry CO_2, water only, or wet CO_2). Next, the bounds for the parameters to be estimated are listed. The identity and structure of the parameters and bounds listed in the files appears in each configuration file in comments (denoted by "#").

For this version of *Sorbentfit*, it is possible to use constant values for any of the parameters and run the fitting with the remaining. This is indicated to *Sorbentfit* via the configuration file by placing the desired values of the parameters in the configuration file in place of a range.

If a simulation run references parameters from a previous fitting, enter the simulation number from which the parameter data was acquired. The second line in the configuration file is where these simulation numbers should be entered. The line should begin with a hash and if more than one simulation is referenced, the simulations should be delimited with spaces.

To have *Sorbentfit* simulate dry cases, in the configuration file the bounds for the dry parameters must be entered, and the parameters for water and humid set to "0." In addition to this the filelist file must have the path to the data files relating to the dry case. To simulate water cases, the process is similar, the configuration must have the bounds for the water parameters entered while the other cases are set to "0," and the filelist file must contain the path to the data files pertaining to water.

Table 2: Default Parameter Bounds (PSO)

Default Parameter Bounds			
Parameter	**Low**	**High**	**Case**
ΔH_c (J/mol)	-110000.00	-35000.00	Dry
ΔS_c (J/mol-K)	-300.00	-150.00	
$\Delta H^{\ddagger}_c$ (J/mol)	10000.00	80000.00	
$\log_{10}(\zeta_z)$	-2.00	5.00	
n_V (mol/m^3)	1500.00	2800.00	Water
ΔH_h (J/mol)	-80000.00	-20000.00	
ΔS_h (J/mol-K)	-300.00	-150.00	
$\Delta H^{\ddagger}_h$ (J/mol)	0.00	70000.00	
$\log_{10}(\zeta_z)$	-5.00	6.00	
ΔH_b (J/mol)	-150000.00	-40000.00	Humid
ΔS_b (J/mol-K)	-300.00	-100.00	
$\Delta H^{\ddagger}_b$ (J/mol)	30000.00	120000.00	
$\log_{10}(\zeta_z)$	-5.00	5.00	

Output

For the fitting routines, the main output appears in two places, the console and an output file created by the program. The output file is named “optresultsX.” For the fitting routines, X is a unique number that serves as the ID for the fitting run. The output that appears in console can be suppressed by adding the “> /dev/null” after the run command. This output appears dynamically during the run, with two lines produced at every iteration of the Particle Swarm Optimizer. The first line displays the iteration number, the minimum cost, and the maximum cost; whereas the second line produces the optimum parameter values associated with that iteration. The order of the parameters corresponds with the list above.

For the fitting routines (at convergence), simulated TGA output appears in the subfolder “results,” with each file named “dataX_Y.” For both the fitting routines and parametric studies, the “Y” refers to the file appearing in “filelist,” in order of appearance, with the counter starting at “0.”

The rows of the output files “dataX_Y” contain the following information:

CO_2 Pressure (Pa) | H_2O Pressure (Pa) | Temperature (K) | Time (s) | Calculated Weight Fraction | Experimental Weight Fraction

Parametric Run (OpenMP Only)

The parametric run uses a list of parameters sets and passes the sets to the model producing simulation results. This routine uses the configuration, filelist, and data files used in the PSO analysis. However, one more file is required. This file is named "paramset.txt." The file contains rows of sets of parameters. The order is the same as the configuration file.

Output

The output of this routine provides two results. The first result is a console output, which displays which parameter set the routine is on. The second result is the simulation data files for each parameter set.

Bayesian Analysis (OpenMP Only)

The second way to estimate the parameters is to use Bayesian Analysis. The procedure for this analysis is as follows. First the routine is ran for so many steps (i.e., 10,000 steps). Analyze the results to see if burn in is achieved. If not continue until burn in is achieved. After burn in is achieved, run the routine for another 10,000 steps. Check for convergence. This is done by using a batch means test to see if the posterior has converged. If converged, the resulting posterior is from the burn in cut to the end. If not converged, run the routine for another set of steps until convergence is achieved.

Configuration File

The configuration file is an important file located in the main folder. This file contains all 13 parameters that *Sorbentfit* can use for parameter optimization and simulation of dry, water, and humid cases. This file contains settings for the ODE solver (which may be left in their default configuration) such as the time step and convergence tolerances, followed by the total pressure in the TGA chamber and the sorbent density. The next line asks for the number of MCMC steps and the file I/O counter. The file I/O counter controls the interval of steps in which file I/O is performed. The lines to follow control the parameters. Next, the bounds for the parameters to be estimated are listed, along with the starting point and standard deviation of the proposal distribution for the parameter. These parameters can be tuned. The ideal acceptance rate is 50% (however 25%–75% is acceptable). If the acceptance rate is too low, decrease the standard deviation. If the acceptance rate is too high, increase the standard deviation. The identity and structure of the parameters and bounds listed in the files appears in each configuration file in comments (denoted by "#").

If a simulation run references parameters from a previous fitting, enter the simulation number from which the parameter data was acquired. The second line in the configuration file is where these simulation numbers should be entered. The line should begin with a hash and if more than one simulation is referenced, the simulations should be delimited with spaces.

Table 3: Default Parameter Bounds (Bayesian)

Default Parameter Bounds			
Parameter	**Low**	**High**	**Standard Deviation**
ΔH_c (J/mol)	-110000.00	-35000.00	300
ΔS_c (J/mol-K)	-300.00	-150.00	1
$\Delta H^{\ddagger}_c$ (J/mol)	10000.00	80000.00	800
$\log_{10}(\zeta_z)$	-2.00	5.00	.5
n_V (mol/m^3)	1500.00	2800.00	50
ΔH_h (J/mol)	-80000.00	-20000.00	700
ΔS_h (J/mol-K)	-300.00	-150.00	1
$\Delta H^{\ddagger}_h$ (J/mol)	0.00	70000.00	700
$\log_{10}(\zeta_z)$	-5.00	6.00	0.5
ΔH_b (J/mol)	-150000.00	-40000.00	400
ΔS_b (J/mol-K)	-300.00	-100.00	2
$\Delta H^{\ddagger}_b$ (J/mol)	30000.00	120000.00	800
$\log_{10}(\zeta_z)$	-5.00	5.00	.6
Observation Error	Nu=2	Tau=.0002	N/A

Output

For the Bayesian Analysis, the main output appears in two places, the console and in two output files created by the program. The first output file is named "BaysParamResults_X." This contains the results for each step (posterior for parameters, observation error per data file, ln (likelihood), and percent error per data file). The columns are as follows:

ΔH_c | ΔS_c | $\Delta H^{\neq}_c$ | $\log_{10}(\zeta_z)$ | n_v | ΔH_h | ΔS_h | $\Delta H^{\neq}_h$ | $\log_{10}(\zeta_z)$ | ΔH_b | ΔS_b | $\Delta H^{\neq}_b$ | $\log_{10}(\zeta_z)$ | observation error (per data file) | ln (likelihood) | % error (per data file)

The second file is "BaysStatResults_X" that contains the acceptance rates of all 13 parameters. This can be used to help "tune" the proposals. The X is a unique number that serves as the ID for the fitting run. The output that appears in console can be suppressed by adding the "> /dev/null" after the run command. This output appears dynamically during the run, which is displayed every time file I/O takes place. The first line displays the current step the routine is on; whereas the second line displays the overall acceptance rate for proposals. The next lines are the percent error per data file.

For the Bayesian Analysis (at each file I/O count), simulated TGA output appears in the subfolder "results," with each file named "dataX_Z_Y." Y refers to the file appearing in "filelist," in order of appearance, with the counter starting at 0. Z corresponds to the step number.

The rows of the output files "dataX_Z_Y" contain the following information:

CO_2 Pressure (Pa) | H_2O Pressure (Pa) | Temperature (K) | Time (s) | Calculated Weight Fraction | Experimental Weight Fraction

3.0 INSTALLATION

3.1 MPI

3.1.1 Dependencies and Platforms

The MPI package requires an MPI implementation (Open MPI – www.open-mpi.org –suffices, as well as any other standard MPI implementation such as MPIch, LAM, or the Microsoft® Cluster Compute Pack) and the BOOST C++ libraries (www.boost.org). All of these packages are open source and free. The package was developed and tested on UNIX-like platforms.

3.1.2 Compilation on UNIX-Like Platforms (including Mac OSX)

Unzip and extract the archive in its permanent location (alternatively, the entire folder can be moved after compilation). Navigate to the top directory of the package. With the dependencies installed, the fitting routines can be compiled by invoking:

```
mpic++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ src/empfit.cpp -o Sorbentfit -lm
```

Sorbentfit can be run with:

```
mpirun -np $ ./Sorbentfit
```

where: "$" is the number of processors.

Note: It may be necessary to add the following to the compilation commands if the compiler cannot find the boost libraries:

```
-L/path/to/my/boostlibraries
```

3.2 OpenMP

3.2.1 Dependencies and Platforms

The OpenMP package requires the BOOST C++ libraries (www.boost.org) and a compiler that supports the OpenMP standard (such as GCC). BOOST is a free and open source package, and most modern compilers support OpenMP. This package was developed and tested on Windows-based and UNIX-like platforms.

3.2.2 Compilation on UNIX-Like Platforms (including Mac OSX)

Unzip and extract the archive in its permanent location (alternatively, the entire folder can be moved after compilation). Navigate to the top directory of the package. The following examples use the GNU compiler GCC. With the dependencies installed,

Compilation of Executable	
PSO	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ src/empfit_TGA.cpp -o empfit_TGA –lm –fopenmp –std=c++11
Parametric Run	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ src/param_set_TGA.cpp -o ParRun –lm –fopenmp –std=c++11
Bayesian Analysis	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ src/bayes_cal_TGA.cpp -o bayes_cal_TGA –lm –fopenmp –std=c++11
Execution of Program	
PSO	./empfit_TGA
Parametric Run	./ParRun
Bayesian Analysis	./bayes_cal_TGA

Note: It may be necessary to add the following to the compilation commands if the compiler cannot find the boost libraries:

-L/path/to/my/boostlibraries

3.2.3 Use on Windows-Based Platforms

The Windows package comes with both the source code (located in the “src” subdirectory), as well as a precompiled executable. TDM-GCC must be installed on the machine for these programs to run. The executables that control the PSO Analysis, Bayesian Analysis, and the parametric studies can be run from the command line by invoking:

Execution of Program (64-bit)	
PSO	.\empfit_TGA.exe
Parametric Run	.\ParRun.exe
Bayesian Analysis	.\bayes_cal_TGA.exe
Execution of Program(32-bit)	
PSO	.\empfit_TGA_32.exe
Parametric Run	.\ParRun_32.exe
Bayesian Analysis	.\bayes_cal_TGA_32.exe

Sorbentfit (FBM)

4.0 INTRODUCTION

This package contains tools for conducting empirical fitting, Bayesian Analysis, and parametric studying for the Carbon Capture Simulation Initiative (CCSI) first-generation sorbent kinetic model. The fitting routine uses a Particle Swarm Optimizer (PSO) to fit the model to Fixed Bed Reactor data. The output of the routine is a set of model parameters corresponding to the CCSI first-generation 2.0 sorbent model, which represent a best fit (in a least-squares sense) of the model to the data provided. The routine should be appropriate for any amine-based solid sorbent. The Bayesian Analysis (**OpenMP only**) uses a Markov Chain Monte Carlo (MCMC) routine to provide a posterior distribution of parameters, along with quantification of uncertainty.

Additionally, the package provides the capability of evaluating the first-generation 2.0 model for an arbitrary sets of parameters and an arbitrary profile of temperatures and gas compositions.

5.0 THEORY AND USE

5.1 Model Overview

The CCSI first-generation sorbent model is written:

$$\frac{\partial x}{\partial t} = k_c[s^2 p_c - x^2/\kappa_c]$$

$$\frac{\partial a}{\partial t} = k_h[p_h(1-a) - a/\kappa_h] - k_b[sap_c - b(1-a)/\kappa_b]$$

$$\frac{\partial b}{\partial t} = k_b[sap_c - b(1-a)/\kappa_b]$$

$$s = 1 - x - w$$

$$\kappa_z = \exp\left(\frac{\Delta S_z}{R}\right)\exp\left(\frac{-\Delta H_z}{RT}\right)/P$$

$$k_z = \zeta_z \exp\left(\frac{-\Delta H_z^{\ddagger}}{RT}\right)$$

where:

Table 4: Equation Parameters

Variable	Description
x	Carbamate Site Fraction
b	Bicarbonate Site Fraction
a	Adsorbed Water Site Friaction
s	Free Amine Site Fraction
p_c	CO_2 Partial Pressure
p_h	H_2O Partial Pressure
P	Total Pressure
n_v	Number of Amine Sites per Unit Volume
n_h	Number of Water Adsorption Sites
ΔH_z	Formation Enthalpy of Species z
$\Delta H^{\neq}_z$	Activation Energy for Reaction z
ΔS_z	Formation Entropy of Species z
ζ_z	Pre-Exponential Factor for Reaction z

The model considers the chemisorption of CO_2 to form carbamate, the physisorption of water, and the formation of bicarbonate from a gaseous CO_2 molecule and adsorbed water, assuming that the kinetics of each are dominated by a single, ideally-behaved chemical reaction.

In order to model the flow in the bed, darcy's law was used to establish governing equations for the flow of gas in the bed. Below is darcy's law:

$$Q = -MA\frac{dP}{dx}$$

This provides an additional parameter "M" which is the mobility of the gas. This parameter, along with the 14 (Sited densities, activation enthlapies, reaction entropies and enthalpies) from the reaction equations, leads to 15 parameters being estimated.

Usage

The model parameters can be estimated in two ways. First the parameters can be estimated by fitting the model to experimental data. Secondly, the parameters can be estimated through Bayesian Analysis. This is the purpose of *Sorbentfit*. *Sorbentfit* estimates the parameters for CO_2-only, H_2O-only, and CO_2-H_2O mixture cases (including n_v & n_h). Value ranges for the parameters are supplied in the configuration files described below.

Units

All units should be SI.

FBM Data Files and Filelist

The packages depend on Fixed Bed data files located in the subfolder "data." The files pertaining to each type of run (dry CO_2, water-only, and wet CO_2) are listed in text files located in the filelist folder for the OpenMP. In filelist.txt , the first two lines must contain the total number of filenames listed in the file, followed by the numbers "5 3" on the next line, then each filename listed on a separate line, with the string "data/" prepended. For example, a file named "FixedBed1.txt" would be listed "data/FixedBed1.txt."

In the data files, the first line must contain a single number specifying the total number of data lines to follow. Each following line contains the information, which is delimited by spaces:

CO_2 (mol/s) | H_2O (mol/s) | N_2 (mol/s) | Temperature (K) | Time (s) | Pressure Drop (atm) | $\%CO_2$ | $\%H_2O$

The time of the first full line need not be zero, but it is assumed that the sorbent was purged of all CO_2 and water at time t = 0.

The default data files contained in the folder "data" and listed in the "filelist" file are a generated experimental data set for the CCSI sorbent of focus, NETL-32D.

Particle Swarm Optimizer (PSO)

The first way to estimate the parameters is to use the Particle Swarm Optimizer (PSO).

Configuration File

The configuration file is an important file located in the main folder. This file contains all 15 parameters that *Sorbentfit* can use for parameter optimization and simulation of dry, water, and humid cases. This file contains settings for the ODE solver (which may be left in their default configuration) such as the time step and convergence tolerances, followed by the atmospheric pressure temperature, and the sorbent density and porosity. After that, parameters dealing with the bed geometry must be entered. Then the availaible measurements must be turned on. Next, the bounds for the parameters to be estimated are listed. The identity and structure of the parameters and bounds listed in the files appears in each configuration file in comments (denoted by "#").

For this version of *Sorbentfit*, it is possible to use constant values for any of the parameters and run the fitting with the remaining. This is indicated to *Sorbentfit* via the configuration file by placing the desired values of the parameters in the configuration file in place of a range.

If a simulation run references parameters from a previous fitting, enter the simulation number from which the parameter data was acquired. The second line in the configuration file is where these simulation numbers should be entered. The line should begin with a hash and if more than one simulation is referenced, the simulations should be delimited with spaces.

To have *Sorbentfit* simulate dry cases, in the configuration file the bounds for the dry parameters must be entered, and the parameters for water and humid set to "0." In addition to this the filelist file must have the path to the data files relating to the dry case. To simulate water cases, the process is similar, the configuration must have the bounds for the water parameters entered while the other cases are set to "0," and the filelist file must contain the path to the data files pertaining to water.

Table 5: Default Parameter Bounds (PSO)

Default Parameter Bounds			
Parameter	**Low**	**High**	**Case**
ΔH_c (J/mol)	-110000.00	-35000.00	Dry
ΔS_c (J/mol-K)	-300.00	-150.00	
$\Delta H^{\ddagger}_c$ (J/mol)	10000.00	80000.00	
$\log_{10}(\zeta_z)$	-2.00	5.00	
n_V (mol/m^3)	1500.00	2800.00	
ΔH_h (J/mol)	-80000.00	-20000.00	Water
ΔS_h (J/mol-K)	-300.00	-150.00	
$\Delta H^{\ddagger}_h$ (J/mol)	0.00	70000.00	
$\log_{10}(\zeta_z)$	-5.00	6.00	
n_h (mol/m^3)	1500.00	2900.00	
ΔH_b (J/mol)	-150000.00	-40000.00	Humid
ΔS_b (J/mol-K)	-300.00	-100.00	
$\Delta H^{\ddagger}_b$ (J/mol)	30000.00	120000.00	
$\log_{10}(\zeta_z)$	-5.00	5.00	

Output

For the fitting routines, the main output appears in two places, the console and an output file created by the program. The output file is named “optresultsX.” For the fitting routines, X is a unique number that serves as the ID for the fitting run. The output that appears in console can be suppressed by adding the “> /dev/null” after the run command. This output appears dynamically during the run, with two lines produced at every iteration of the Particle Swarm Optimizer. The first line displays the iteration number, the minimum cost, and the maximum cost; whereas the second line produces the optimum parameter values associated with that iteration. The order of the parameters corresponds with the list above.

For the fitting routines (at convergence), simulated Fixed Bed output appears in the subfolder “results,” with each file named “dataX_Y.” For both the fitting routines and parametric studies, the “Y” refers to the file appearing in “filelist,” in order of appearance, with the counter starting at “0.”

The rows of the output files “dataX_Y” contain the following information:

CO_2 (mol/s) | H_2O (mol/s) | N_2 (mol/s) | Temperature (K) | Time (s) | Pressure Drop (atm | $\%CO_2$ | $\%H_2O$ |

Calculated (| Pressure Drop (atm) | $\%CO_2$ | $\%H_2O$ |)

Parametric Run (OpenMP Only)

The parametric run uses a list of parameters sets and passes the sets to the model producing simulation results. This routine uses the configuration, filelist, and data files used in the PSO analysis. However, one more file is required. This file is named "Paramset_FBM.txt." The file contains rows of sets of parameters. The order is the same as the configuration file.

Output

The output of this routine provides two results. The first result is a console output, which displays which parameter set the routine is on. The second result is the simulation data files for each parameter set.

Bayesian Analysis (OpenMP Only)

The second way to estimate the parameters is to use Bayesian Analysis. The procedure for this analysis is as follows. First the routine is ran for a set number of steps (i.e., 10,000 steps). Analyze the results to see if burn in is achieved. If not continue until burn in is achieved. After burn in is achieved, run the routine for another 10,000 steps. Check for convergence. This is done by using a batch means test to see if the posterior has converged. If converged, the resulting posterior is from the burn in cut to the end. If not converged, run the routine for another set of steps until convergence is achieved.

Configuration File

The configuration file is an important file located in the main folder. This file contains all 15 parameters that *Sorbentfit* can use for parameter optimization and simulation of dry, water, and humid cases. This file contains settings for the ODE solver (which may be left in their default configuration) such as the time step and convergence tolerances, followed by the atmospheric pressure temperature, and the sorbent density and porosity. After that, parameters dealing with the bed geometry must be entered. Then the availaible measurements must be turned on. The lines to follow control the parameters. Next, the bounds for the parameters to be estimated are listed, along with the starting point and standard deviation of the proposal distribution for the parameter. These parameters can be tuned. The ideal acceptance rate is 50% (however 25%–75% is acceptable). If the acceptance rate is too low, decrease the standard deviation. If the acceptance rate is too high, increase the standard deviation. After all parameter information is entered, the next two lines are the priors for the observational error per data set (ie Pressure drop, CO2, or H2O). The next line asks for the number of MCMC steps and the file I/O counter. The file I/O counter controls the interval of steps in which file I/O is performed. The identity and structure of the parameters and bounds listed in the files appears in each configuration file in comments (denoted by "#").

If a simulation run references parameters from a previous fitting, enter the simulation number from which the parameter data was acquired. The second line in the configuration file is where these simulation numbers should be entered. The line should begin with a hash and if more than one simulation is referenced, the simulations should be delimited with spaces.

Table 6: Default Parameter Bounds (Bayesian)

Default Parameter Bounds			
Parameter	**Low**	**High**	**Standard Deviation**
ΔH_c (J/mol)	-130000.00	-35000.00	1500
ΔS_c (J/mol-K)	-350.00	-150.00	40
$\Delta H^{\ddagger}_c$ (J/mol)	10000.00	80000.00	800
$\log_{10}(\zeta_z)$	-2.00	5.00	.025
n_V (mol/m^3)	1500.00	2800.00	15
ΔH_h (J/mol)	-80000.00	-20000.00	2000
ΔS_h (J/mol-K)	-300.00	-100.00	25
$\Delta H^{\ddagger}_h$ (J/mol)	0.00	70000.00	100
$\log_{10}(\zeta_z)$	-5.00	6.00	0.07
n_h (mol/m^3)	1500.00	2800.00	50
ΔH_b (J/mol)	-150000.00	-40000.00	28000
ΔS_b (J/mol-K)	-300.00	-100.00	210
$\Delta H^{\ddagger}_b$ (J/mol)	30000.00	120000.00	28000
$\log_{10}(\zeta_z)$	-5.00	5.00	5.1
Observation Error (Pressure drop)	Nu=2	Tau=1e-8	N/A
Observation Error (% outlet)	Nu=2	Tau=.08	N/A

Output

For the Bayesian Analysis, the main output appears in three places, the console and in two output files created by the program. The first output file is named "BayesParamResults_X." This contains the results for each step (posterior for parameters, ln (likelihood), and percent error per data file). The columns are as follows:

ΔH_c | ΔS_c | $\Delta H^{\neq}_c$ | $\log_{10}(\zeta_z)$ | n_v | ΔH_h | ΔS_h | $\Delta H^{\neq}_h$ | $\log_{10}(\zeta_z)$ | ΔH_b | ΔS_b | $\Delta H^{\neq}_b$ | $\log_{10}(\zeta_z)$ | ln (likelihood) | % error (per data file)

The second file is "BayesStatResults_X" that contains the acceptance rates of all 15 parameters. This can be used to help "tune" the proposals. The last file is the "BayesPsiResults_X" file that contains the observational error tunning values per data set. The X is a unique number that serves as the ID for the fitting run. The output that appears in console can be suppressed by adding the "> /dev/null" after the run command. This output appears dynamically during the run, which is displayed every time file I/O takes place. The first line displays the current step the routine is on; whereas the second line displays the overall acceptance rate for proposals. The next lines are the percent error per data file.

For the Bayesian Analysis (at each file I/O count), simulated Fixed Bed output appears in the subfolder "results," with each file named "dataX_Z_Y." Y refers to the file appearing in "filelist," in order of appearance, with the counter starting at 0. Z corresponds to the step number.

The rows of the output files “dataX_Z_Y” contain the following information:

CO_2 (mol/s) | H_2O (mol/s) | N_2 (mol/s) | Temperature (K) | Time (s) | Pressure Drop (atm) | %CO_2 | %H_2O |
Calculated (| Pressure Drop (atm) | %CO_2 | %H_2O |)

6.0 INSTALLATIONOPENMP

6.1.1 Dependencies and Platforms

The OpenMP package requires the BOOST C++ libraries (www.boost.org), Eigen C++ libraries (eigen.tuxfamily.org) and a compiler that supports the OpenMP standard (such as GCC). BOOST is a free and open source package, and most modern compilers support OpenMP. This package was developed and tested on Windows-based and UNIX-like platforms.

6.1.2 Compilation on UNIX-Like Platforms (including Mac OSX)

Unzip and extract the archive in its permanent location (alternatively, the entire folder can be moved after compilation). Navigate to the top directory of the package. The following examples use the GNU compiler GCC. With the dependencies installed,

Compilation of Executable	
PSO	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ -I/path/to/eigen/ src/empfit_FBM.cpp -o empfit_FBM –lm –fopenmp –std=c++11
Parametric Run	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ -I/path/to/eigen/ src/param_set_FBM.cpp -o ParRun_FBM –lm –fopenmp –std=c++11
Bayesian Analysis	g++ -O4 -DNDEBUG -I/path/to/boost_X_XX_X/ -I/path/to/eigen/ src/bayes_cal_FBM.cpp -o bayes_cal_FBM –lm –fopenmp –std=c++11
Execution of Program	
PSO	./empfit_FBM
Parametric Run	./ParRun_FBM
Bayesian Analysis	./bayes_cal_FBM

Note: It may be necessary to add the following to the compilation commands if the compiler cannot find the boost libraries:

-L/path/to/my/boostlibraries

6.1.3 Use on Windows-Based Platforms

The Windows package comes with both the source code (located in the “src” subdirectory), as well as a precompiled executable. TDM-GCC must be installed on the machine for these programs to run. The executables that control the PSO Analysis, Bayesian Analysis, and the parametric studies can be run from the command line by invoking:

Execution of Program (64-bit)	
PSO	.\empfit_FBM.exe
Parametric Run	.\ParRun.exe
Bayesian Analysis	.\bayes_cal_FBM.exe
No 32-bit support	

7.0 REPORTING ISSUES

To report an issue with this package send an e-mail to ccsi-support@acceleratecarboncapture.org.