Review and analysis of CO2 photoreduction kinetics

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A walk through of mean median multi-start trust-region method for estimating nonlinear CO2 photoreduction kinetic model coefficients

Number of pages = 11

Number of figures = 3

See excellent MATLAB documentation for more information for the trust-region method

https://uk.mathworks.com/help/optim/ug/constrained-nonlinear-optimization-algorithms.html

MATLAB R2018b used

Data reported by Tan

L.-L. Tan, W.-J. Ong, S.-P. Chai and A. R. Mohamed, Chemical Engineering Journal, 2017, 308, 248–255

- Extracted CH4 data at different partial pressures of CO2 from Figure 3 (a) using WebPlotDigitizer
- Extracted CH4 data at different partial pressures of H2O from Figure 3 (b) using WebPlotDigitizer

Copy and paste these settings to run the script below

(Partial pressure CO2 (bar), partial pressure H2O (bar), CH4 production (umol.gcat-1.h-1), I (mW/cm2),

reported model coefficients and constraints used for mean median model in order of: k, alpha,

KH2O and KCO2)

experimental_settings_PCO2 = [0 0.25 0.5 0.75 0.9 1.01];

experimental_settings_PH2O = 0.043;

reported_CH4_production = [0 0.172 0.202 0.212 0.385 0.336];

I = 81;

reported_coefficients = [84.42 4.4E-2 8.070 1.93E-2];

lower_constraint = [0 0 0 0];

upper_constraint = [100 0.5 30 0.5];

Or use following if partial pressure CO2 was kept constant

experimental_settings_PCO2 = 0.9;

experimental_settings_PH2O = [0 0.043 0.088 0.173 0.312 0.565];

reported_CH4_production = [0 0.385 0.389 0.431 0.329 0.310];

I = 81;

reported_coefficients = [84.42 4.4E-2 8.070 1.93E-2];

lower_constraint = [0 0 0 0];

upper_constraint = [100 0.5 30 0.5];

Data reported by Tahir

M. Tahir and N. S. Amin, Chemical Engineering Journal, 2013, 230, 314–327

- Extracted CH4 data at different partial pressures of CO2 from Figure 12 using WebPlotDigitizer
- Assumed yield reported was for ten hour reaction

Copy and paste these settings to run the script below

(Partial pressure CO2 (bar), partial pressure H2O (bar), CH4 production (umol.gcat-1.h-1), I (mW/cm2),

reported model coefficients and constraints used for mean median model in order of: k, alpha,

KH2O and KCO2)

experimental_settings_PCO2 = [0 0.019 0.039 0.059 0.079];

experimental_settings_PH2O = 0.0432;

reported_CH4_production = [0 67.70 77.48 73.47 65.29];

I = 150;

reported_coefficients = [500 6.0E-1 7.5E-1 30];

lower_constraint = [0 0 0 0];

upper_constraint = [200 0.8 25 50];

Data reported by Khalizadeh

A. Khalilzadeh and A. Shariati, Solar Energy, 2018, 164, 251–261

- Extracted CH4 data at different partial pressures of CO2 from Figure 10 (a)
- Extracted CH4 data at different partial pressures of H2O from Figure 10 (b)

Copy and paste these settings to run the script below

(Partial pressure CO2 (bar), partial pressure H2O (bar), CH4 production (umol.gcat-1.h-1),

I (mW/cm2), reported model coefficients and constraints used for mean median model

in order of: k, alpha, KH2O, KCO2 and n)

experimental_settings_PCO2 = [0 0.28 0.55 0.76 1.01];

experimental_settings_PH2O = 0.155;

reported_CH4_production = [0 19.84 23.53 28.15 24.92];

I = 85;

reported_coefficients = [6.47 6.5E-1 145.2 22.74 1.23];

lower_constraint = [0 0 0 0 0];

upper_constraint = [80 0.7 200 40 2];

Or use following if partial pressure CO2 was kept constant

experimental_settings_PCO2 = 0.76;

experimental_settings_PH2O = [0.043 0.095 0.155 0.250 0.310];

reported_CH4_production = [22.15 24.92 28.15 26.30 22.61];

I = 85;

reported_coefficients = [6.47 6.5E-1 145.2 22.74 1.23];

lower_constraint = [0 0 0 0 0];

upper_constraint =[80 0.7 200 40 2];

Please enter data and experimental settings used to fit the model

```
% Copy and paste experimental settings, production data and reported coeffients
% as code - highlight text and click "Code" icon in "LIVE EDITOR" ribbon
experimental_settings_PCO2 = [0 0.25 0.5 0.75 0.9 1.01];
experimental_settings_PH2O = 0.043;
reported_CH4_production = [0 0.172 0.202 0.212 0.385 0.336];
I = 81;
reported_coefficients = [84.42 4.4E-2 8.070 1.93E-2];
lower_constraint = [0 0 0 0];
upper_constraint = [100 0.5 30 0.5];
```

Line changes optional - Assign two site LH and Sips kinetic model functions

```
if numel(experimental_settings_PH2O) == 1
    pressure_settings = ones(numel(experimental_settings_PCO2),2);
    pressure_settings(:,1) = pressure_settings(:,1).*experimental_settings_PCO2';
    pressure_settings(:,2) = pressure_settings(:,2).*experimental_settings_PH2O;
else
    pressure_settings = ones(numel(experimental_settings_PH2O),2);
```

```
    pressure_settings(:,1) = pressure_settings(:,1).*experimental_settings_PCO2;
    pressure_settings(:,2) = pressure_settings(:,2).*experimental_settings_PH2O';
end

% Two site kinetic model
% b(1) = k, b(2) = alpha, b(3) = KH2O and b(4) = KCO2

Two_site_LH_model = @(b,pressure_settings)...
                    (b(1).*I.^b(2).*(b(3).*pressure_settings(:,2).*b(4).*...
                    pressure_settings(:,1))./...
                    ((1 + (b(3).*pressure_settings(:,2))...
                    + (b(4).*pressure_settings(:,1))).^2);

% Sips kinetic model
% b(1) = k, b(2) = alpha, b(3) = KH2O, b(4) = KCO2 and b(5) = n

Sips_kinetic_model = @(b,pressure_settings)...
                     (b(1).*(I.^b(2))).*(((pressure_settings(:,1).*b(4)).^...
                     (1./b(5))).*((pressure_settings(:,2).*b(3)).^(1./b(5))))...
                     ./((1 + ((pressure_settings(:,1).*b(4)).^(1./b(5))) +...
                     ((pressure_settings(:,2).*b(3)).^(1./b(5)))).^2);
```

Line changes optional - Assign model and variables for plots

- To select model that median multi-start trust-region method will use
- Set number of columns for histogram plot
- Assign plot labels used by histogram and 3D bar plots

```
number_parameters = numel(lower_constraint);

if number_parameters == 4

    % Assign model
    kinetic_model = Two_site_LH_model;

    % Assign number of columns for histogram subplot
    number_columns = 2;

    % Assign plot labels
    x_label = ["k (\mumol.g_{cat}^{-1}.h^{-1})" "\alpha" "K_{H_{2}O}" + ...
               "(bar^{-1})" "K_{CO_2} (bar^{-1})"];

else

    % Assign model
    kinetic_model = Sips_kinetic_model;

    % Assign number of columns for histogram subplot
    number_columns = 3;

    % Assign plot labels
```

```
    x_label = ["k (\mumol.g_{cat}^{-1}.h^{-1})" "\alpha" "K_{H_{2}O}" + ...
               "(bar^{-1})" "K_{CO_2} (bar^{-1})" "n"];

end
```

Please enter values

- For number of loops median multi-start trust -region method will run
- Number of iterations per median loop
- Number of multi-start points

```
% Set the number of times the median iteration method will loop, Set to 1 if
% you are not interested in calculating the standard deviation of the
% median values and only want one set of median coefficient estimates
number_for_std_deviation_calculation = 10;

% Set the number times the multi-start trust-region method will iterate
% within number of loops set above
number_median_iterations = 50;

% Set number of starting points for multi-start algorithm
no_multi_start_points = 10;
```

Line changes optional - Median multi-start trust-region method

- This is the median multi-start trust-region method
- After each multi-start iteration, the median of the coefficients estimated will be saved in an array

```
% Assign empty data array to record the median value after each loop of
% multi-start trust-region iterations is complete
multiple_median_approach_values = [];
all_multistart_values = [];

% Assign empty data array to record the coefficient estimates for each
% multi-start solution
multistart_model_values        = [];


for std_deviation_run = 1:number_for_std_deviation_calculation

    for median_run = 1:number_median_iterations

        % Randomly select intial starting point values between upper and
        % lower constraint values
        Random_starting_point_values = (upper_constraint-lower_constraint)....
                                        *rand(1,1) + lower_constraint;

        problem = createOptimProblem('lsqcurvefit','x0',...
```

```
                                    Random_starting_point_values,'objective',...
                                    kinetic_model,'lb',lower_constraint,...
                                    'ub',upper_constraint,'xdata',...
                                    pressure_settings,'ydata',...
                                    reported_CH4_production');

        ms = MultiStart('Display','off');
        [xmulti,errormulti,flagm,outptm,manyminsm] = run(ms,problem,...
                                                    no_multi_start_points);

        multistart_model_values(median_run,1:numel(lower_constraint)) = xmulti;

    end

 % Lets collect the coefficient values based on median approach for each round
 multiple_median_approach_values(std_deviation_run,...
 1:numel(lower_constraint)) = median(multistart_model_values);

 % Let's collect all of the multistart values for plotting histograms later
 all_multistart_values = [all_multistart_values;multistart_model_values];

end
```

Line changes optional - What is the mean and standard deviation of

coefficients from the median multi-start approach?

In order of k, alpha, KH2O and KCO2 for two site and k, alpha, KH2O, KCO2 and n for Sips

Repeat the 'Line changes optional - Median multi-start trust-region method' and this chunk of code to see that the method is reproducible

```
% Calculate mean and standard deviation of coefficients from median
% multi-start approach

if number_for_std_deviation_calculation == 1
    disp(['Not enough median values to calcuate standard deviation' ...
          ' and mean. Set ''number_for_std_deviation_calculation" > 1'])
    disp(['Coefficient values from median approach after' ...
          ' one iteration loop used  shown below:'])
    mean_median_coefficients = multiple_median_approach_values
else
    disp('The standard deviation of the median coefficients are:')
    std_dev_median_coefficients = std(multiple_median_approach_values)
    disp('The mean of the median coefficients are:')
    mean_median_coefficients    = mean(multiple_median_approach_values)
end
```

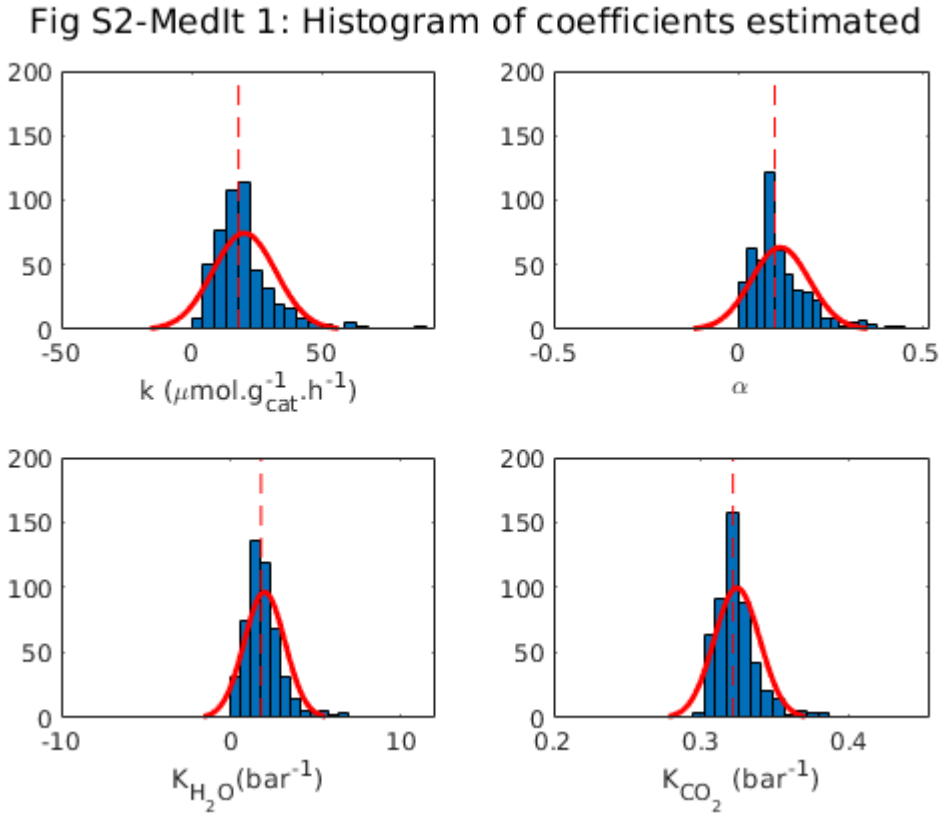
```
The standard deviation of the median coefficients are:
std_dev_median_coefficients = 1×4
    0.7613    0.0086    0.1277    0.0016
The mean of the median coefficients are:
```

```
mean_median_coefficients = 1×4
   18.0480    0.0998    1.7783    0.3211
```

Line changes optional - Plot histograms of the coefficient values with mean median value as dotted red line

```
figure;

% Set maximum histogram plot height, will need to increase for higher
% values set for: 'number_for_std_deviation_calculation' and/or
% 'number_median_iterations'
max_height=200;

% Plot histogram and median line for k coefficient estimates
subplot(2,number_columns,1);
histfit(all_multistart_values(:,1),20); xlabel(x_label(1), 'FontSize', 20);
hold on
p = line([mean_median_coefficients(1,1),mean_median_coefficients(1,1)],...
         [0,max_height],'Color','r','LineStyle','--');

% Plot histogram and median line for alpha coefficient estimates
subplot(2,number_columns,2);
histfit(all_multistart_values(:,2),20); xlabel(x_label(2), 'FontSize', 20);
hold on
p = line([mean_median_coefficients(1,2),mean_median_coefficients(1,2)],...
         [0,max_height],'Color','r','LineStyle','--');

% Plot histogram and median line for KH2O coefficient estimates
subplot(2,number_columns,3);
histfit(all_multistart_values(:,3),20); xlabel(x_label(3), 'FontSize', 20);
hold on
p = line([mean_median_coefficients(1,3),mean_median_coefficients(1,3)],...
         [0,max_height],'Color','r','LineStyle','--');

% Plot histogram and median line for KCO2 coefficient estimates
subplot(2,number_columns,4);
histfit(all_multistart_values(:,4),20); xlabel(x_label(4), 'FontSize', 20);
hold on
p = line([mean_median_coefficients(1,4),mean_median_coefficients(1,4)],...
         [0,max_height],'Color','r','LineStyle','--');

if numel(x_label) == 5

    % Plot histogram and median line for n coefficient estimates
    subplot(2,number_columns,5);
    histfit(all_multistart_values(:,5),20); xlabel(x_label(5), 'FontSize', 20);
    hold on
    p = line([mean_median_coefficients(1,5),mean_median_coefficients(1,5)],...
             [0,max_height],'Color','r','LineStyle','--');

end
```

```
sgtitle('Fig S2-MedIt 1: Histogram of coefficients estimated')
```

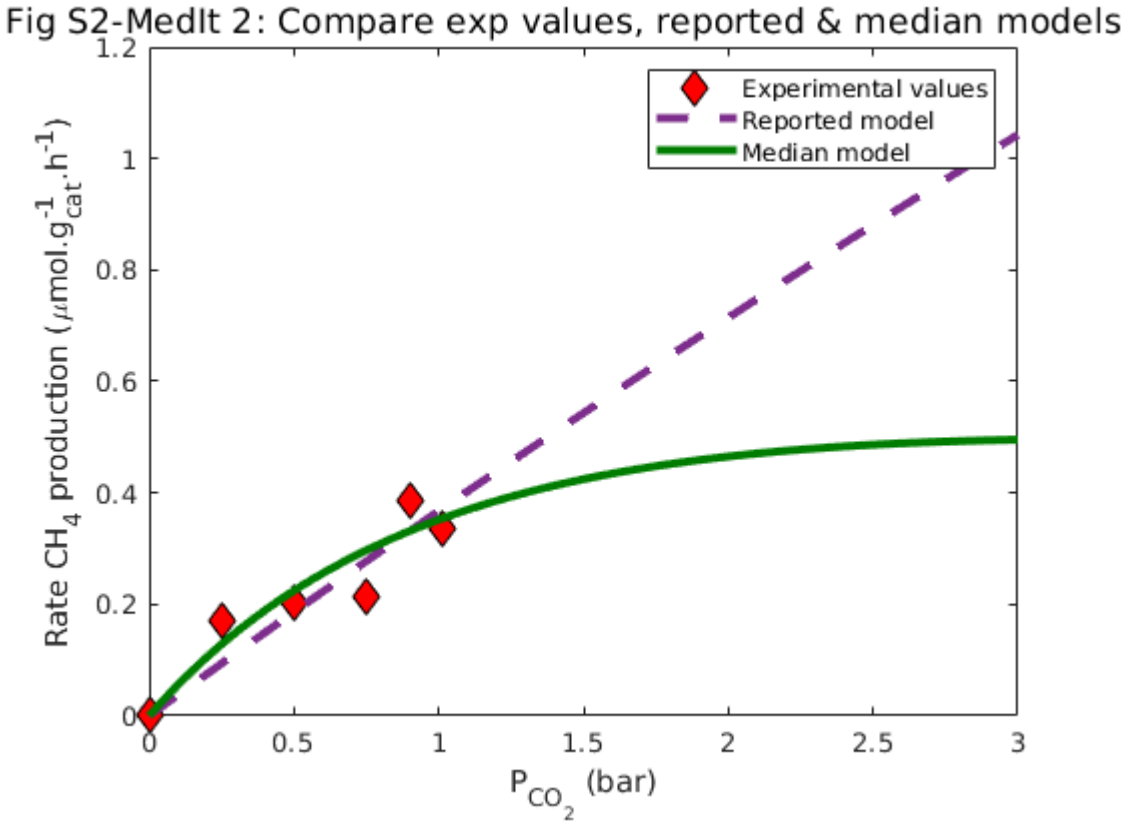


Line changes optional - Plot the mean median model, recorded model and recorded data points

```
if numel(experimental_settings_PH2O) == 1

    % Create CO2 partial pressure values to fit with models
    model_settings_PCO2 = linspace(0,3,100)';

    % Use constant experimental H2O partial pressure setting to fit with
    % model
    model_settings_PH2O = ones(numel(model_settings_PCO2),1).*...
                                experimental_settings_PH2O;

    % Combine CO2 and H2O partial pressures into matrix to fit with model
    model_pressure_settings = [model_settings_PCO2 model_settings_PH2O];

    % Estimate CH4 production using reported and mean median models
    CH4_production_reported_model = kinetic_model(reported_coefficients,...
                                                  model_pressure_settings);
    CH4_production_median_model   = kinetic_model(mean_median_coefficients,...
                                                  model_pressure_settings);

    % Plot experimental values, reported and mean median model
```

```
    figure;
    plot(experimental_settings_PCO2,reported_CH4_production,...
        'Color', 'r','Marker','diamond','LineStyle','none','MarkerSize',10,...
        'MarkerFaceColor','r','MarkerEdgeColor','k')
    hold on;
    plot(model_settings_PCO2, CH4_production_reported_model,...
        'Color',[0.4940, 0.1840, 0.5560],'Marker','none','LineStyle','--',...
        'LineWidth',3)
    hold on;
    plot(model_settings_PCO2, CH4_production_median_model,...
        'Color', [0, 0.5, 0],'Marker','none','LineStyle','-','LineWidth',3)
    legend('Experimental values', 'Reported model','Median model');

    xlabel('P_{CO_2} (bar)','FontWeight','bold')
    ylabel('Rate CH_4 production (\mumol.g_{cat}^{-1}.h^{-1})','FontWeight',...
           'bold')

else

    % Create H2O partial pressure values to fit with models
    model_settings_PH2O = linspace(0,1,100)';

    % Use constant experimental CO2 partial pressure setting to fit with
    % model
    model_settings_PCO2 = ones(numel(model_settings_PH2O),1).*...
                               experimental_settings_PCO2;

    % Combine CO2 and H2O partial pressures into matrix to fit with model
    model_pressure_settings = [model_settings_PCO2 model_settings_PH2O];

    % Estimate CH4 production using reported and mean median models
    CH4_production_reported_model = kinetic_model(reported_coefficients,...
                                                  model_pressure_settings);
    CH4_production_median_model   = kinetic_model(mean_median_coefficients,...
                                                  model_pressure_settings);

    % Plot experimental values, reported and mean median model
    figure;
    plot(experimental_settings_PH2O,reported_CH4_production,...
        'Color', 'r','Marker','diamond','LineStyle','none','MarkerSize',10,...
        'MarkerFaceColor','r','MarkerEdgeColor','k')
    hold on;
    plot(model_settings_PH2O, CH4_production_reported_model,...
        'Color',[0.4940, 0.1840, 0.5560],'Marker','none','LineStyle','--',...
        'LineWidth',3)
    hold on;
    plot(model_settings_PH2O, CH4_production_median_model,...
        'Color', [0, 0.5, 0],'Marker','none','LineStyle','-','LineWidth',3)
    legend('Experimental values', 'Reported model','Median model');
    xlabel('P_{H_{2}O} (bar)','FontWeight','bold')
    ylabel('Rate CH_4 production (\mumol.g_{cat}^{-1}.h^{-1})','FontWeight',...
            'bold')
```

```
end
sgtitle('Fig S2-MedIt 2: Compare exp values, reported & median models')
```



Line changes optional - How do the estimated reported and mean median model coefficient estimates compare?

```
figure;
bar3([reported_coefficients;mean_median_coefficients])
xticklabels(x_label)
yticklabels({'Reported model', 'Median model'})
zlabel('Coefficient value')
sgtitle('Fig S2-MedIt 3: Compare reported & median coefficients')
```

Fig S2-MedIt 3: Compare reported & median coefficients