DYNAMIC BEHAVIOUR OF PROCESS SYSTEMS
Modelling, Simulation, Optimisation, Parameter Estimation of an Isothermal CSTR

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1. Dynamic Model

Table 1: CSTR Model in tabular form

Equation	No. Eqn	New Vbls	No. Vbls	Assumptions
$\frac{dN_i}{dt} = F_{in}^1 \cdot x_{in,i}^1 + F_{in}^2 \cdot x_{in,i}^2 - F_{out} \cdot x_i - v_i \cdot r \cdot w$	3	$N_i, F_{in}^1, F_{in}^2, F_{out}, x_i, r$	10	No nuclear reaction, Perfect mixing
$x_i = \frac{N_i}{N_T}$	3	N_T	1	
$N_T = \sum N_i$	1			
$r = \frac{k_r \cdot \left(P_{CO} \cdot P_{H_2}^2 - {}^1/_{K_{eq}} \cdot P_{CH_3OH}\right)}{\left(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{CH_3OH} \cdot P_{CH_3OH}\right)^3}$	1	$P_{CO}, P_{H_2}, P_{CH_3OH}$	3	
$P_i = x_i \cdot P$	3	P	1	
$F_{out} = \frac{V_p \cdot c_v}{\sqrt{T}} \cdot (P - P_{atm})$	1	V_p	1	Isothermal
$P \cdot V = N_T \cdot R \cdot T$	1			Ideal gas behaviour, Fixed Volume
Total	**13**		**16**	

The no nuclear reaction assumption implies conservation of mass. We assume perfect mixing in the reactor because we are using a CSTR. This allows us to use x_i throughout the reactor (including the outlet). The isothermal assumption allows us to treat the temperature as constant throughout the reactor and the outlet. Ideal gas behaviour can be used because the reaction involves only gases, which allows us to implement the ideal gas law. We assume fixed volume because the gasses take up the entire volume in the CSTR, allowing us to treat the volume as constant.

Table 2: Notation table

Symbol	Definiton	Units
$\mathbf{N_i}$	Holdup of i	kmol
$\mathbf{F_{in}^1}$	Inlet flowrate 1	kmol/h
$\mathbf{x_{in,i}^1}$	Inlet 1 molar fraction of i	
$\mathbf{F_{in}^2}$	Inlet flowrate 2	kmol/h
$\mathbf{x_{in,i}^2}$	Inlet 2 molar fraction of i	
$\mathbf{F_{out}}$	Molar flowrate (out)	kmol/h
$\mathbf{x_i}$	Molar fraction of i	
$\mathbf{v_i}$	Stoichiometric coefficient of i	
$\mathbf{r}$	Rate of reaction	kmol/kg-cat·h
$\mathbf{w}$	Weigh of catalyst	kg-cat
$\mathbf{N_T}$	Total holdup	kmol
$\mathbf{k_r}$	Rate constant	$\mathrm{kmol \cdot kg - cat^{-1} \cdot h^{-1} \cdot kPa^{-3}}$
$\mathbf{K_{eq}}$	Equilibrium constant	$\mathrm{kPa^{-2}}$
$\mathbf{K_{CO}}$	CO constant	$\mathrm{kPa^{-1}}$
$\mathbf{K_{H_2}}$	H_2 constant	$\mathrm{kPa^{-1}}$
$\mathbf{K_{CH_3OH}}$	CH_3OH constant	$\mathrm{kPa^{-1}}$
$\mathbf{P_{CO}}$	Partial pressure of CO	kPa
$\mathbf{P_{H_2}}$	Partial pressure of H_2	kPa
$\mathbf{P_{CH_3OH}}$	Partial pressure of CH_3OH	kPa
$\mathbf{P}$	Reactor pressure	kPa
$\mathbf{V_p}$	Normalised valve position	
$\mathbf{c_v}$	Valve constant	$\mathrm{kmol \cdot h^{-1} \cdot T^{0.5} \cdot kPa^{-1}}$
$\mathbf{T}$	Temperature	K
$\mathbf{P_{atm}}$	Atmospheric pressure	kPa
$\mathbf{V}$	Volume of reactor	$\mathrm{m^3}$
$\mathbf{R}$	Ideal gas constant	$\mathrm{m^3 \cdot kPa \cdot K^{-1} \cdot kmol^{-1}}$

2. gPROMS Implementation

Done on gPROMS using *CSTR* as the model and *Q2* as the process. The value of c_v obtained is:

$$c_v = 3.2505 \cdot 10^{-4}\ \text{kmol} \cdot \text{h}^{-1} \cdot \text{T}^{0.5} \cdot \text{kPa}^{-1}$$

3. Steady-state Analysis

The simulation was done on gPROMS using *CSTR* as the model and *Q3* as the process. The graphs were made using gRMS. Four separate graphs are depicted here in order to show the behavior of the key variables.

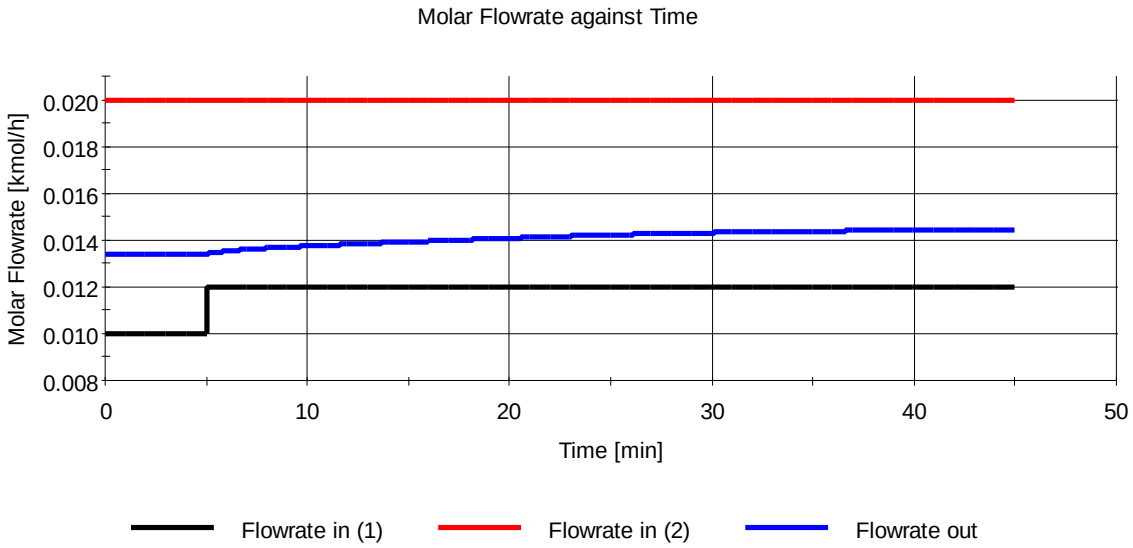


Figure 1:Molar Flowrate against Time

The inlet flowrate 1 (flowrate of CO) increases by 20% at t = 5min. This does not cause a step increase in the outlet flowrate. The outlet flowrate steadily increases as the reaction progresses.

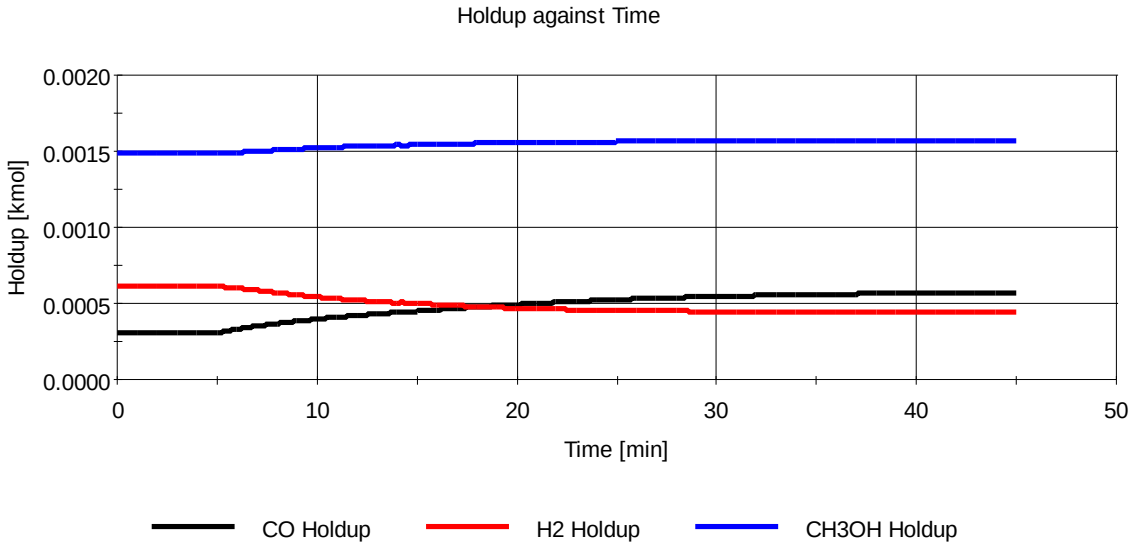


Figure 2: Holdup against Time

The amount of CO in the reactor begins to increase when the inlet flowrate of CO increases. This causes more of the H_2 to be consumed and more CH_3OH to be produced. The holdup of each of the compounds plateaus as time progresses (reaction approaches equilibrium).

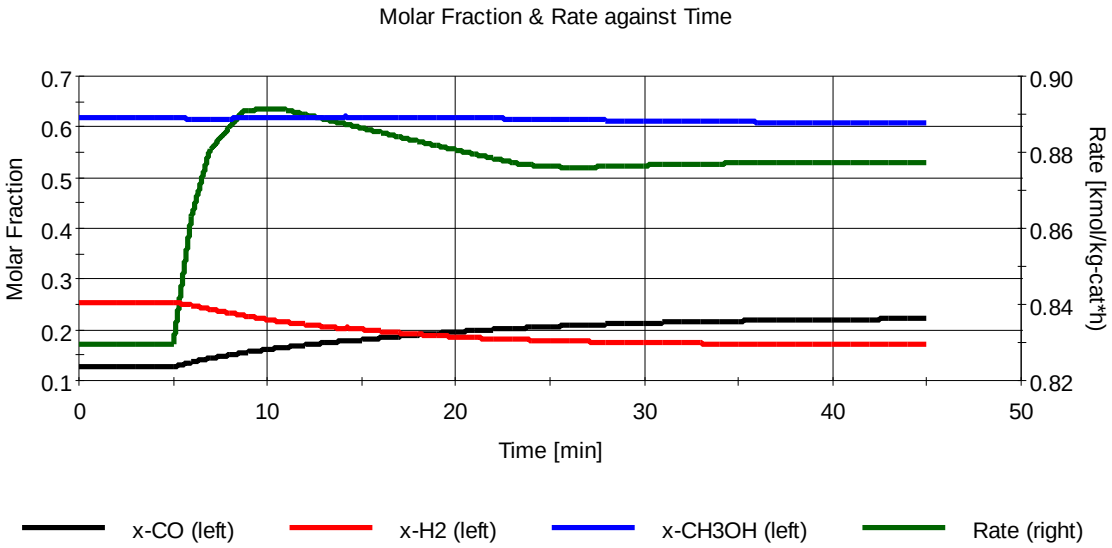


Figure 3: Molar Fraction against Time

The mole fraction of CO in the reactor increases while that of H_2 decreases. The mole fraction of CH_3OH does not vary much because the holdup of CH_3OH does not change much relative to the total holdup. The rate of the reaction increases rapidly when the CO feed is increased, reaching a maximum at around t = 10.5min. The rate then becomes steady as time progresses further (approaches equilibrium).

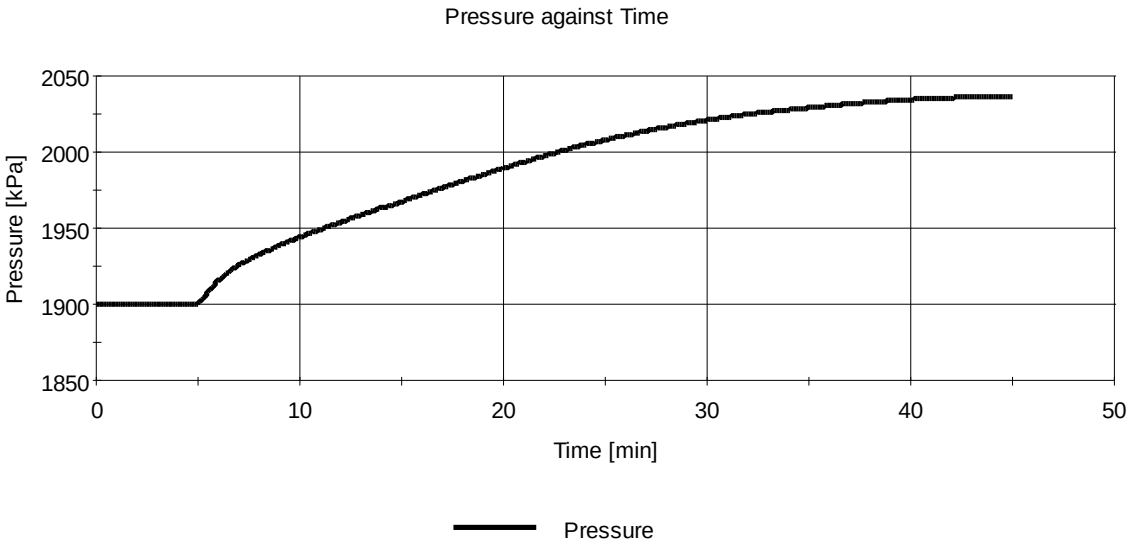


Figure 4: Pressure against Time

The pressure inside the reactor increases as soon as the flow of carbon monoxide is increased. It increases rapidly and then slows down as the reactor approaches equilibrium once again. A parallel between the rate of reaction and the change in pressure can be made. When the rate is increasing rapidly so is the pressure, as the rate becomes stable, the pressure also becomes stable. Physically the change in pressure inside the reactor can be attributed to the increase in total moles within the reactor. This can be said because we assume that the ideal gas law can be used (relating N_T and P).

4. PI Controller

The simulation was done on gPROMS using *Controller* as the model and *Q4* as the process. The graphs were made using gRMS.

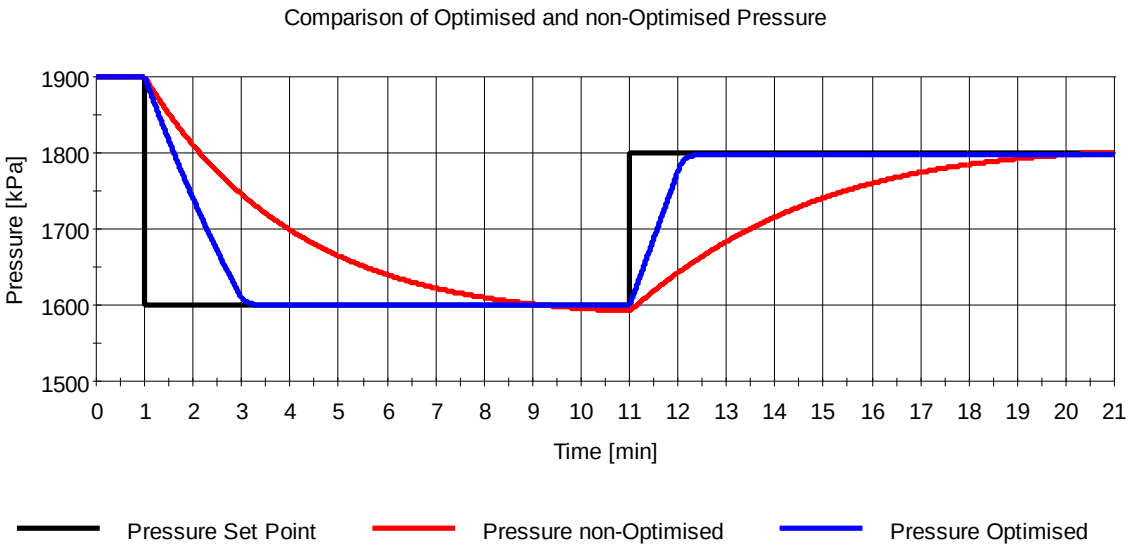


Figure 5: Pressure against Time

The behavior of the non-optimised and optimised controllers can be seen above. The non-optimised controller displays an Integral Square (ISE) of 3207 $kPa^2 \cdot h$. It is quite accurate as a controller but takes a long time to reach its set point. It takes approximately 8 mins to reach the 1600 kPa set point, and it overshoots slightly, and takes approximately 10 mins to reach the 1800 kPa set point. The optimal values of K_c and τ_i were found to be 0.02499 kPa^{-1} and 1 h respectively. The optimised controller has a better ISE of 1187 $kPa^2 \cdot h$. The optimised controller acts a lot faster and does not experience an overshoot. The optimised controller reaches the 1600 kPa set point in just over 2 mins and the 1800 kPa set point in just over 1 min. The controller could potentially be further improved by loosening the bounds on τ_i, because it is on its upper bound.

5. Optimising k_r

A model validation was done on gPROMS using *ParameterEstimation* as the model and *Q5* as the process to obtain a new estimation of k_r.

$$k_r = 1.03732\ \text{kmol} \cdot \text{kg} - \text{cat}^{-1} \cdot \text{h}^{-1} \cdot \text{kPa}^{-3}$$

Using the new estimated value, profiles for pressure, molar fraction of carbon monoxide and molar fraction of methanol were predicted and compared to measured values:

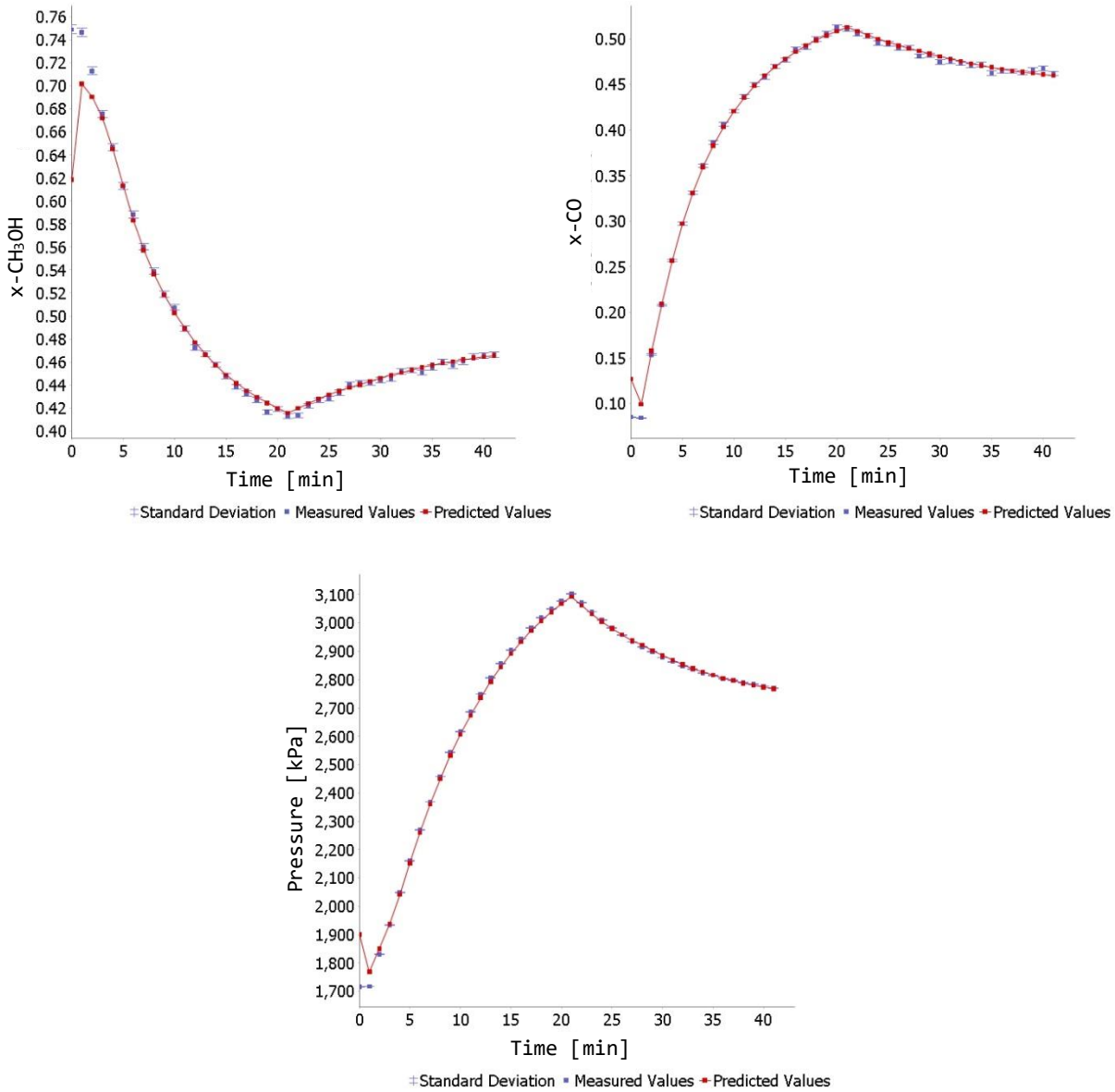


Figure 6: Comparison between measured and predicted values, for the molar fraction of CH_3OH and CO and for the Pressure

Apart from the first 2-3 minutes there is good agreement between the predicted and measured values for pressure, molar fraction of CH_3OH and molar fraction of CO. Perhaps the start is difficult to model with this value of k_r. From 21 minutes onward there is not as close an agreement between the predicted and measured values of the molar fractions (CO and CH_3OH), with the predicted value often being outside the standard deviation of the measured values.

*Table 3: Results of goodness of fit test for Q5. * indicates this value does not satisfy the null hypothesis*

Fitted Parameter	χ^2	χ^2 Critical
P	39394.9*	56.9424
X-CO	11076.4*	56.9424
X-CH3OH	1462.88*	56.9424
Total	51934.2*	152.094

Goodness of fit test. A chi-squared (χ^2) test is used to compare the weighted residual and the expected weighted residual - when the null hypothesis true, the difference between them is 0. Clearly, the null hypothesis is not met meaning that the difference between the weighted residual and expected weighted residual is not 0. In lay-man terms the accuracy of the predicted values compared to the measured values is low and therefore the estimation is not accurate.

*Table 4: Results of Lack of fit test for Q5. * indicates this value does not satisfy the null hypothesis*

Fitted Parameter	F-Value	F-Critical
P	959.852*	1.67476
X-CO	10.6913*	1.67476
X-CH3OH	76.6910*	1.67476
Total	944.468*	1.34268

Lack of fit test. This test compares the error in the model with that of the measurement. The null hypothesis is that the error due to lack of fit is equal to the pure error. This hypothesis is not proven, hence the model has inherent error.

Table 5: Table of confidence intervals, bounds and statistical values

Model parameter		Final Value	Initial Guess	Lower Bound	Upper Bound	Confidence Interval 90%	Confidence Interval 95%	Confidence Interval 99%	95% t-value	Standard deviation
k_r	[kmol/kgcat*h*kPa^3]	1.03732	0.50000	0.05000	5.00000	0.00195350	0.00233349	0.00308439	444.537	0.00117913
									Reference t-value (95%):	1.65674

The 99% confidence interval is very small compared to the final value indicating that the distribution of values for k_r is tight as shown by the standard deviation. This is further reinforced by the 95% t-value being greater than the 95% reference t-value indicating that the certainty in the estimation with the inputs given is high. Given that we know the predicted values do not fit the measured values well, but there is certainty in the parameter estimation, it can be theorized that other parameters lack accuracy.

6. Optimising k_r, K_{CO}, K_{H2}, and K_{CH3OH}

The model validation was done on gPROMS using *ParameterEstimation* as the model and *Q6* as the process to obtain a new value of k_r, K_{CO}, K_{H2}, and K_{CH3OH}.

$$k_r = 1.26844\ \text{kmol} \cdot \text{kg} - \text{cat}^{-1} \cdot \text{h}^{-1} \cdot \text{kPa}^{-3}$$

$$K_{CO} = 0.165054\ \text{kPa}^{-1}$$

$$K_{H_2} = 0.291953\ \text{kPa}^{-1}$$

$$K_{CH_3OH} = 0.12\ \text{kPa}^{-1}$$

*Table 6: Table of confidence intervals, bounds and statistical values for Q6. * indicates that the value is on its upper bound*

Model parameter		Final Value	Initial Guess	Lower Bound	Upper Bound	Confidence Interval 90%	95%	99%	95% t-value	Standard deviation
K_{CO}	[kPa^{-1}]	0.165054	0.15000	0.12000	0.18000	0.00275035	0.00328503	0.00434196	50.2444	0.00165912
K_{H2}	[kPa^{-1}]	0.291953	0.35000	0.28000	0.42000	0.00997979	0.119199	0.0157550	24.4929	0.00602021
K_{CH3OH}	[kPa^{-1}]	0.120000	0.10000	0.08000	0.12000*	-	-	-	-	-
k_r	[kmol/kgcat*h*kPa^3]	1.26844	0.50000	0.05000	5.00000	0.0496140	0.0592591	0.0783251	21.4050	0.0299291
								Reference t-value (95%):		1.65771

The estimation of K_{CH3OH} is at its upper bound meaning that a better estimate may exist beyond this and loosening this bound might result in even better estimates for the other paramters. The confidence bounds for K_{CO}, K_{H2} and k_r are all relatively small and the 95% t-value is above the reference t-value indicating a high level of certainty in the estimations. The confidence bounds for K_{CH3OH} are not available because its value is on its upper bound. The value of k_r is not too far away from the value estimated in Q5, however the confidence intervals have widened.

The confidence interval ellipsoids are represented on the following graphs.

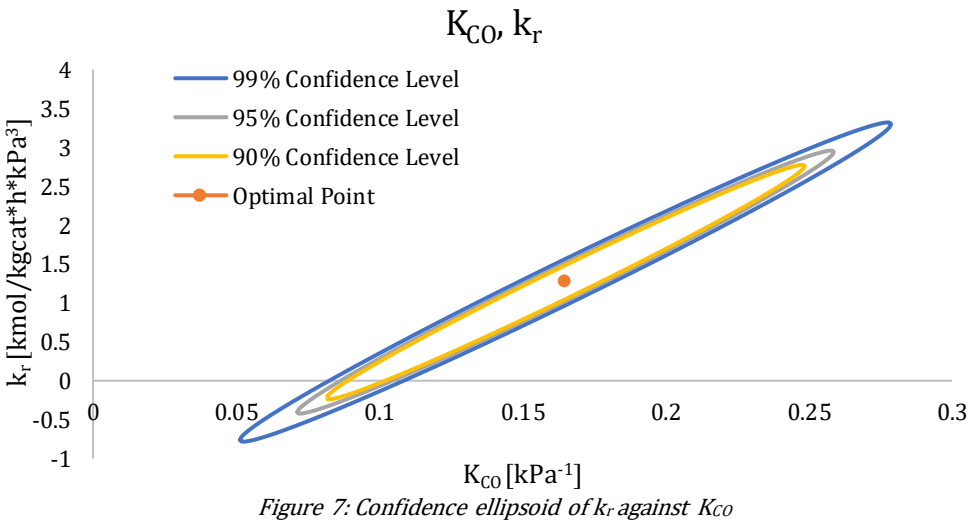


Figure 7: Confidence ellipsoid of k_r against K_{CO}

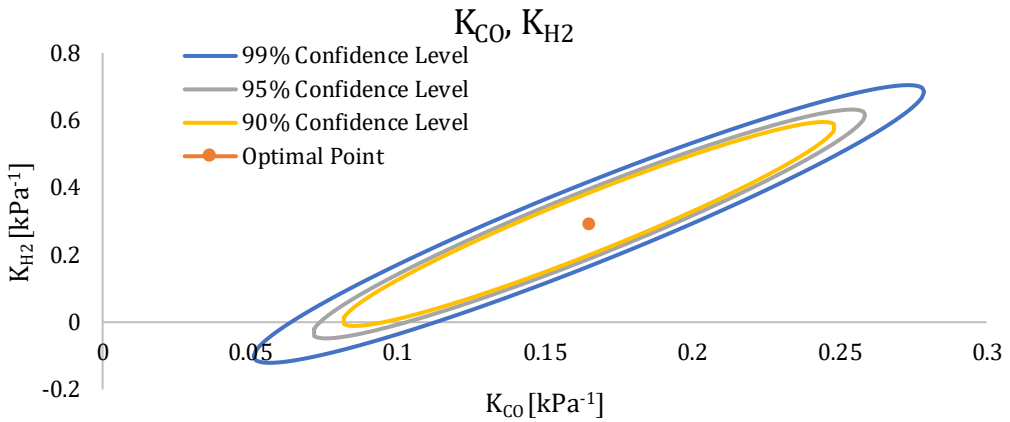


Figure 8: Confidence ellipsoid of K_{H2} against K_{CO}

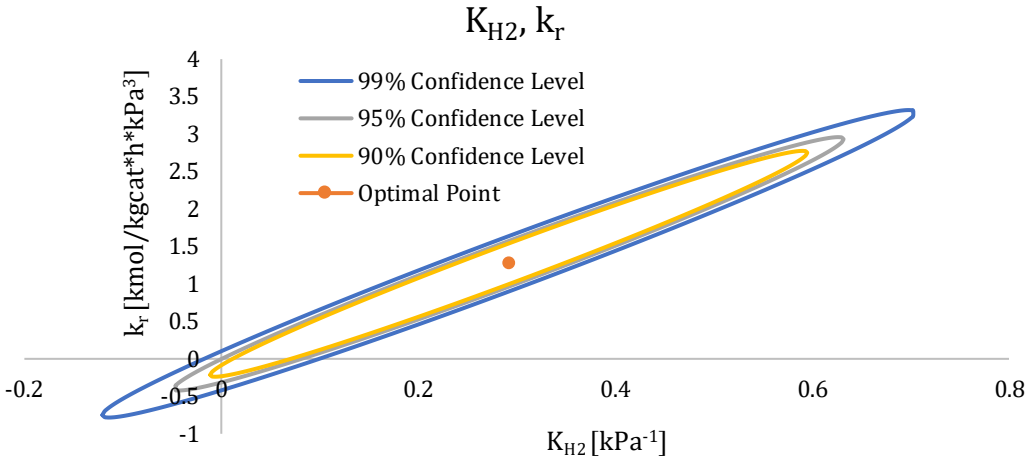
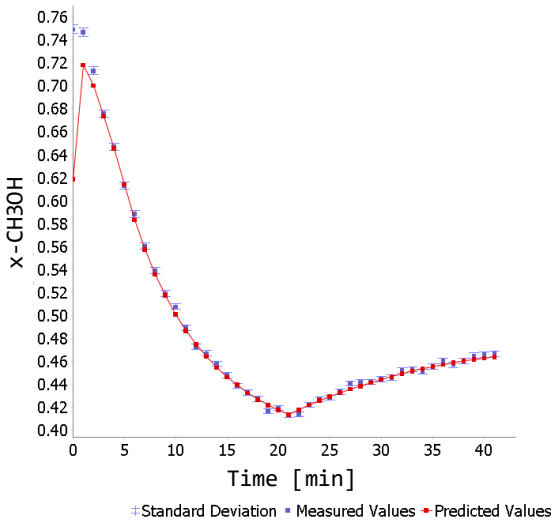
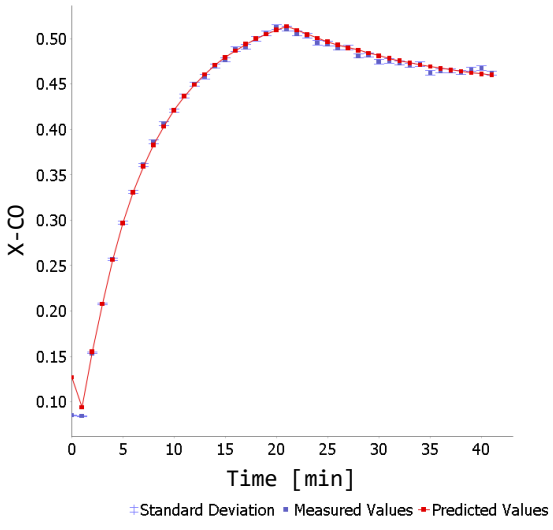


Figure 9: Confidence ellipsoid of k_r against K_{H2}

The accuracy of the estimations are in general low. In particular, there is a huge variation in k_r between approximately 3.5 and -0.6. K_{H2} is also inaccurate, while K_{CO} is actually more accurate than the other 2 estimations with a smaller variation range. For K_{H2} and K_{CO}, the 90% confidence bounds extend past the expected ±20% deviation. Additionally, K_{H2}, K_{CO} and k_r are highly correlated to each other, indicated by the elongated shape of the ellipsoids. The reason for the high level of correlation is due to the fact that all 3 parameters appear only in the rate equation which means that changes in one parameter can be compensated by changes in another and different combinations of these parameters will give the same rate of reaction.





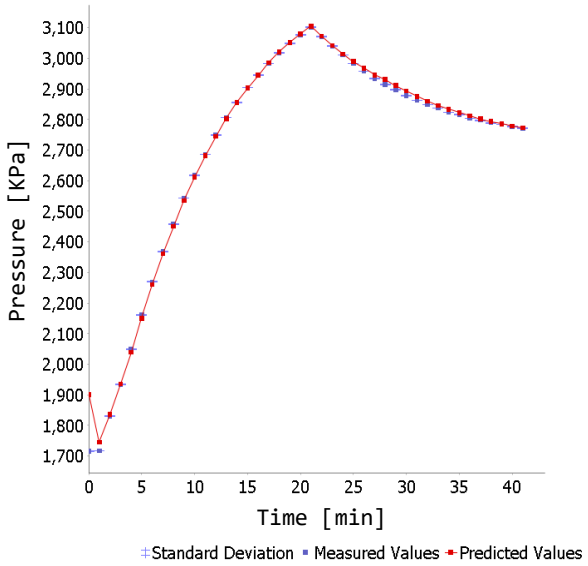


Figure 10: Comparison between measured and predicted values, for the molar fraction of CH_3OH and CO and for the Pressure

The situation is very similar to Q5. For the first 2-3 minutes all 3 graphs show a huge deviation from measured values, then for roughly 20 minutes the measured and predicted values match well after which the predicted mole fractions do not match the measured values.

*Table 7: Results of goodness of fit test for Q6. * indicates this value does not satisfy the null hypothesis*

Fitted Parameter	χ^2	χ^2 Critical
P	36787.1*	53.3835
X-CO	10299.9*	53.3835
X-CH3OH	1339.39*	53.3835
Total	48426.4*	148.779

Goodness of fit test. As before, a chi-squared (χ^2) test is used to compare the weighted residual and the expected weighted residual - while the null hypothesis true, the difference between them is 0. The null hypothesis is not met meaning that the difference between the weighted residual and expected weighted residual is not 0 i.e. the estimations are not accurate. The χ^2 values for Q6 are marginally lower than in Q5 indicating a marginal gain in accuracy.

*Table 8: Results of Lack of fit test for Q6. * indicates this value does not satisfy the null hypothesis*

Fitted Parameter	F-Value	F-Critical
P	967.081*	1.68718
X-CO	11.0540*	1.68718
X-CH3OH	76.1835*	1.68718
Total	903.591*	1.34472

Lack of fit test. This test compares the error in the model with that of the measurement. The null hypothesis is that the error due to lack of fit is equal to the pure error. This hypothesis is not proven, hence the model has inherent error.

Further actions can be taken to improve the accuracy of the model. Firstly, loosening the bounds on K_{CH3OH}, which is on its upper bound, might aid in finding better estimates and increase accuracy which would be indicated on the chi-squared test. Secondly, the model assumed the ideal gas equation is

suitable, however, this equation of state might not model this process well under these high pressures and so a different equation of state might result in greater accuracy. Finally, more experiments can be run to increase the number of measurements and improve the accuracy of the estimations.