Kinetic modeling of liquefied petroleum gas (LPG) reduction of titania in MATLAB

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Abstract. In the present study, reduction of Titania (TiO₂) by liquefied petroleum gas (LPG)-hydrogen-argon gas mixture was investigated by experimental and kinetic modelling in MATLAB. The reduction experiments were carried out in the temperature range of 1100-1200°C with a reduction time from 1-3 hours and 10-20 minutes of LPG flowing time. A shrinking core model (SCM) was employed for the kinetic modelling in order to determine the rate and extent of reduction. The highest experimental extent of reduction of 38% occurred at a temperature of 1200°C with 3 hours reduction time and 20 minutes of LPG flowing time. The SCM gave a predicted extent of reduction of 82.1% due to assumptions made in the model. The deviation between SCM and experimental data was attributed to porosity, thermodynamic properties and minute thermal fluctuations within the sample. In general, the reduction rates increased with increasing reduction temperature and LPG flowing time.

Keywords: Titania, LPG, Kinetic Modelling, MATLAB, Shrinking Core Model, Titanium Carbide

1. Introduction
Titanium-containing compounds are very important in the advance technologies especially in the field of aerospace and biomedical. Commercially, titania was reduced into metallic titanium and titanium based compounds such as titanium carbide and nitride which have applications in catalyst, paint pigment or manufacture of composite materials [1]. The current technology used for production of metallic titanium through the Kroll process is by chlorination of titania at high temperature at about 800°C-1100°C [2]. According to Adipuri et al. [3], chlorination of titanium oxycarbide (TiOₓC₁₋ₓ) occurs at much lower temperature, around 400-500°C than TiO₂ in the production of titanium tetrachloride through the Kroll process. Synthesis of TiOₓC₁₋ₓ can be introduced through different technologies. It is mainly produced by reduction of titania with carbon in the temperature range of 1700 to 2000°C [4]. Studies by Dewan et al. [5] have shown that carbothermal reduction of titania in different gas atmosphere was significant and it was found that hydrogen reduced titania and reacted with carbon to form methane gas. This methane gas promoted the formation of titanium sub oxides which was reduced into TiOₓC₁₋ₓ. For this paper, synthesis of TiOₓC₁₋ₓ by liquefied petroleum gas (LPG) could have few advantages such as the replacement of the coal as the reducing agent. Besides this, a low CO₂ emission can be achieved.
compared to conventional reduction and being environmentally friendly by reusing natural gas which is abundant in Malaysia [6].

2. Experimental Setup
The experimental setup is shown in Figure 1. Raw material was titania powder with an average particle size of about 3.71 µm supplied by Alfa Aesar, USA. The sample mass was 1.0 gram for each reduction experiment. The reduction experiments were carried out in a reactor tube furnace which was purged with a mixture of commercial liquefied petroleum gas (LPG), hydrogen and high-purity argon as gaseous reductants. The gas mixtures was 10/45/45 vol. % of LPG-H₂-Ar gas. Reduction was carried out between 1100-1200°C for 1-3 hours. LPG gas analysis by gas chromatography have shown its composition to be composed of 69.9 vol. % propane (C₃H₈) and 28.7 vol. % butane (C₄H₁₀) [7]. At high temperature, all of the C₃H₈ and C₄H₁₀ will be converted to CH₄ due to presence of TiO₂ as a catalyst and thermodynamic stability of CH₄ at the reduction temperature used [8]. All gases were supplied by Goldenair Industrial Supply Sdn. Berhad, Malaysia. The total gas flow rate was maintained at 1.5 Liter/min.

![Figure 1. Schematic flow sheet of gas system (1) Regulator with flow meter, (2) gas splitter, (3) gas flow rate gauge (LPM), (4) reactor tube furnace](image)

3. Experimental
TiO₂ reduction data for the kinetic modelling work has been published by Yin et al. [9]. Besides this, experimental data by Sheikh Abdul Rezan et al. [11] was also used in the kinetic model. The reduction mechanism of TiO₂ by H₂ follows a shrinking core model (SCM) as proven by the latter studies. For methane (CH₄) reduction of TiO₂, studies by Guangqing Zhang et al. [12, 13] have shown the SCM model gives a good representation of the kinetics.

4. Kinetic Modelling Methodology
The kinetic model was coded using MATLAB R2011b software based on the SCM. Details on the MATLAB model have been reported elsewhere [10, 14]. In order to solve the complicated equations regarding CH₄ reduction of TiO₂ in the kinetic model, step by step modelling process was done based on its mass and thermal transport properties [15]. The kinetic model developed by MATLAB in this study has been successfully applied previously on isothermal and non-isothermal reduction of TiO₂ and Fe₂O₃ in H₂ gas atmosphere [10, 14, 22]. A flowchart on the computational methodology in the SCM is given in Figure 2.
4.1 Determination Rate of Transfer

Consider the chemical reaction in Eq. 1, it was assume TiO$_2$ is a solid spherical reactant metallic oxide compound, CH$_4$ is the reactant gas, TiC is the solid reaction product and CO with H$_2$ is the evolved gaseous product. The evolved gas product was mainly H$_2$ since CO content was less than 1 vol. % [9]. The overall reaction can be described by Eq. 2 with the symbol D designated as the product gas mixture of CO and H$_2$. Since LPG gas concentration was 10 vol.% whereas H$_2$ gas was 45 vol. %, the CO gas concentration could be ignored as it was less than 1 vol. % due to the small TiO$_2$ pellet mass. If gaseous transport away from the pellet was defined to be positive magnitude in nature, the rates of mass transport for n$_A$(CH$_4$) and n$_B$(H$_2$) for ideal gas behavior was represented by Eq. 3-4.

TiO$_2$ + 3CH$_4(g)$ = TiC + 2CO$_{(g)}$ + 6H$_2(g)$

\[ \Delta G^\circ = -0.157^\circ T + 145.3 \text{ (kcal/mol)} \]  

(1)

TiO$_2$ + 3CH$_4(g)$ = TiC + 2CO$_{(g)}$ + 6H$_2(g)$, A$_{(s)}$ + B$_{(g)}$ = C$_{(s)}$ + D$_{(g)}$

where $A$ = TiO$_2(s)$, $B$ = CH$_4(g)$, $C$ = TiC$_{(s)}$ and $D$ = CO$_{(g)}$ & H$_2(g)$ combined

(2)
\[ n_A = \frac{4\pi R_0^2}{R} K_m \left( \frac{PCH_4(s)}{T_s} - \frac{PCH_4(o)}{T_g} \right) \]

\[ n_B = \frac{4\pi R_0^2}{R} K_m \left( \frac{P(H_2)(s)}{T_s} - \frac{P(H_2)(o)}{T_g} \right) \]

where \( K_m \) = Mass transfer coefficient (cm/sec), \( R \) = Gas constant of 82.05 atm. cm\(^3\)/g-mole-° K, \( P_A(a) \) = Pressure of reactant gas in atmosphere, \( P_B(a) \) = Pressure of product gas in atmosphere and \( a \) = surface (s) or bulk (o) gas.

### 4.2 Prediction of Convective Mass Transfer Coefficients

The convective mass transfer coefficient between a gas and a particle with spherical shape was calculated from Eq. 5-6,

\[ Sh = 2.0 + (Re)^{1/2}(Sc)^{1/3} \]

\[ Sh = \frac{K_m \times d_o}{D_{AB}} \]

where Sherwood number, \( Sh \) is a function of the mass Reynolds number (Re), Schmidt number (Sc), and binary diffusivity (\( D_{AB} \)). AB was the reductant and product gas defined as CH\(_4\)-H\(_2\).

### 4.3 Prediction of Binary Diffusivity

The method was based on kinetic theory and gives predictions with an average deviation of 4 pct. (%) with a maximum deviation of 16% [16]. The binary diffusivity \( \beta_{AB} \) (cm\(^2\)/sec) prediction was made using Eq. 7.

\[ \beta_{AB} = BT^{3/2} \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \sqrt{\frac{1}{P \times (r_{AB})^2 \times ID}} \]

where \( r_{AB} \) = collision diameter (Å), taken as the mean of the collision diameters of components A (CH\(_4\)) and B (H\(_2\)), \( M_1, M_2 \) = molecular weights of CH\(_4\) and H\(_2\), \( B = [10.7 - 2.46\sqrt{(1/M_A + 1/M_B)}] \times 10^4 \), \( ID \) = Collision integral of diffusion (unitless), \( P \) = absolute pressure (atm) and \( T \) = Temperature (K). The symbol A & B was designated as the main reductant-product gas.

### 4.4 Prediction of Convective Heat Transfer Coefficients

Equations 8-9 below enables accurate prediction of the convective heat transfer coefficient between a sphere and flowing gas using dimensionless parameter called Nusselt (Nu) number.

\[ Nu = 2.0 + 0.6(Re)^{1/2}(Pr)^{1/3} \]

\[ Nu = \frac{h_c \times d_o}{K_f} \]
where Re = Reynolds number, Pr = Prandtl number, $h_c$ = convective heat transfer coefficient (cal/cm²-sec-°K) and $K_T$ = thermal conductivity of the gas film (cal/sec-cm-°K).

4.5 Determination Rate of Reaction

The location of the reaction interface on the spherical particle determines the reaction points E and F in Eq. 10. These points enable the calculation of $R'$ (% Reduction) or extent of reduction. This, along with the bulk gas composition, evaluation of transport mass coefficients, and the temperatures of the reaction interface and gas stream enables calculations of the instantaneous reaction rate ($n_c$) at any given time during the reaction. The extent of conversion of TiO₂ to TiC was proportional to the magnitude of $n_c$.

$$n_c = \frac{(P_a(o) - K_{eq} \cdot P_a(o))}{T_g \cdot (K_{eq} \left( \frac{E}{D_{A,eff}} + \frac{F}{K_{mA}} \right) + \left( \frac{E}{D_{B,eff}} + \frac{F}{K_{mB}} \right))}$$

(10)

where $E = \frac{R_i(R_o - r_i)}{4\pi(r_i \times R_o)}$ and $F = \frac{R}{4\pi R_o}$ are location points of reaction interface on the sphere, $R$ = final radius, mass transfer coefficient of molecules A and B for gases ( $K_{mA}$, $K_{mB}$), $D_{A,eff}$ and $D_{B,eff}$ are the effective Knudsen diffusion for molecules A and B.

4.6 Determination of Spherical Pellet Temperature

Prediction of the variation of spherical pellet temperature change during reaction was more difficult than the determination of the gaseous mass transport rate. The reasoning behind this argument was that heat transfer at the reactant core consisting of TiO₂ occurred simultaneously with heat transfer through the accumulated solid reaction product (TiC) and the bulk gas. To simplify the heat transfer calculations in MATLAB, a few assumptions was made. The first assumption, the accumulation of heat in reaction zone was negligible. The 2nd assumption, heat transfer was 1-dimensional and by conduction, convection and radiation. The 3rd assumption, the average pellet core temperature of $T_c$ was defined to account for the overall heat transfer away the pellet. This allowed the simplification of the temperature calculations by Eq. 11-14.

$$T_c = \frac{\Delta t \left( n_A C_p A(T_p) \cdot (T_p - T_o) + n_B C_p B(T_p) \cdot (T_p - T_o) - 4\pi K_p (R_o - r_i) \cdot T_z - k_* (r_i) \cdot T_z + T_c \right)_{z-1}}{4\pi R_o \cdot 3 \cdot C_p A(T_p) \cdot \Delta t + 4\pi R_o \cdot 3 \cdot C_p B(T_p) \cdot \Delta t + 4\pi R_o \cdot 3 \cdot C_p A(T_o) \cdot \Delta t}$$

(11)

$$T_p = T_c - \frac{R_o}{(r_i + R_o)} \cdot (T_c - T_s)$$

(12)

$$T_s = \frac{n_A C_p A(T_p) \cdot (T_p - T_o) + n_B C_p B(T_p) \cdot (T_p - T_o)}{4\pi K_p R_o \cdot (R_o - r_i) + 4\pi R_o \cdot 2 \cdot h_c \cdot T_g}$$

(13)

$$T_g = \frac{n_A C_p A(T_r) \cdot (T_r - T_o) + 4\pi R_o \cdot 2 \cdot h_c \cdot T_s + 4\pi R_o \cdot 2 \cdot h_c \cdot T_s}{4\pi R_o \cdot 2 \cdot h_c \cdot T_o + 4\pi R_o \cdot 2 \cdot h_c \cdot T_s}$$

(14)
where \( T_p \) = Average temperature of the particle (°K), \( C_{pp} \) = heat capacity of solid product (calorie/mole-°K), \( C_{pc} \) = heat capacity of solid reactant core (calorie/mole-°K), \( C_{pg} \) = heat capacity of reducing gas (calorie/mole-°K).

The overall chemical reaction for the system was represented by Eq. 2 from SCM [17] and the reaction rate can be predicted by the simultaneous solution of Eq.10-15 done in MATLAB. Lastly, after the reaction rate \( (n_c) \) and time of reaction \( (t) \) have been determined, the \( R' \) can be calculated based on Eq. 15-16:

\[
\Delta t = -4\pi r_i \rho_c \frac{\Delta r}{n_c} \quad (15)
\]

\[
R_o \rho_c = [1 - (1 - R')^\frac{1}{3}] = kt \quad (16)
\]

where \( R' \) = % Reduction (100*instantaneous weight of pellet/ initial weight of pellet sphere), \( R' = \frac{(M_o - M(t))}{(M_o-M_i)} \), \( \rho_c \) = molar density, \( M_o \) = initial weight of pellet (TiO\(_2\)), \( M(t) \) = weight of pellet at time \( t \) (Ti\(_2\)O\(_3\) + TiC), \( M_i \) = final weight of pellet (TiC) and \( k \) = kinetic constant (s\(^{-1}\))

5. Results and discussion

The experimental data for extent of reduction (\( R' \)) versus time at different temperatures is shown in Figure 3. Table 1 tabulates the final \( R' \) calculated from the weight loss of samples. The \( R' \) was increasing with reduction temperature and time because a higher amount of TiO\(_2\) was reduced into Ti\(_2\)O\(_3\) and TiC. As shown in Figure 3, there was significant difference in \( R' \) between higher and lower reduction temperature. At 1200°C and 180 min of reduction time with 20 min LPG flow time, the \( R' \) was the highest at 37.9%. The titania sample reduced at latter conditions contained 3.68 wt.% carbon when analyzed by elemental carbon analysis.

![Figure 3. Reduction of titania by LPG-hydrogen-argon mixture (10 vol. % LPG -45 vol.% H\(_2\)-45 vol. % Argon) at different temperatures and LPG flowing times](image-url)
Table 1. Extents of titania reduction at different temperatures with 20 min of LPG flowing time

| LPG Flowing Time (min) | 10 | 20 |
|------------------------|----|----|
| Temperature, °C        |    |    |
| 1100                   | 60 | 180|
| 1200                   | 60 | 180|
| Reduction Time, min    |    |    |
| 60                     | 180| 180|
| 180                    | 60 | 180|
| Extent of Reduction, % |    |    |
| 12.48                  | 14.98| 16.98| 19.97| 14.98| 17.48| 34.95| 37.96|
| Carbon, wt.%           |    |    |
| 0.97                   | 1.07| 2.05| 2.11| 1.51| 2.40| 2.43| 3.68|

During the reduction process, thermal cracking of propane and butane took place, which is the major component in LPG; propane was cracked into ethane, ethylene, methane, and hydrogen [18, 19]. The final stable state was methane (CH₄). Deposition of solid carbon occurred at the end of the cracking process, as shown in Eq. (17). The presence of carbon monoxide (CO) gas was due to the chemical reaction in Eq. (1).

CH₄(g) → C(s) + 2H₂(g) \hspace{1cm} (17)

The cracking process enhances the rate of reduction as more carbon is available for reduction. Furthermore, similar work done by Itao, G.B. and N.M. Anacleto [6] showed the thermodynamic activity of C₃H₈ and C₄H₁₀ was much higher than CO and H₂. This higher activity allowed a greater degree of cracking into solid carbon. The longer flowing time of LPG was able to produce more free carbon and thus increase the reduction rate. Free solid carbon can reduce and carburize titania into TiC but the reduction was slow due to the low reduction temperature studied in this work.

5.1 Predicted Reduction Kinetics of Titania

The reduction of titania has been one of the most important and complex gas-solid reactions in kinetic study by various researchers [9, 12, 13, 22]. The complexity was due to the formation of titania sub-oxides such as Ti₄O₉, Ti₃O₅ and Ti₂O₃. These sub-oxides affects the reaction rate and differ greatly in terms of its physical and material properties. A shrinking core model (SCM) developed by Szekely et al. [20] was employed to determine the reaction rate. From the mass and heat transport equations listed above, the transport-limited reaction rate for reduction of titania was calculated in MATLAB. Figures 4 show the results of isothermal reduction at 1100°C and 1200°C. From the figure, both rate and extent of reduction increased with temperature from 1100°C to 1200°C.
Figures 5 shows the comparison between the predicted and experimental R’ at 1100°C and 1200°C in LPG-H₂-Ar gas atmosphere. From the figure, the deviation between the predicted and experimental results are significant. All the simulated plots are similar in which the predicted non-isothermal R’ data was closer to the experimental results compared with isothermal conditions. Even though the deviation was significant, it can be observed that the R’ increased with temperature for both simulated and experimental. The source of the deviation will be discussed below.
The comparison of temperature variation with respect to reaction rate was shown in Figure 6. From the figure, it shows the deviation between predicted and experimental measured results. On the other hand, the experimental reaction rate changed linearly with reduction time, which showed the reaction was chemically controlled. In this case, temperature was a key parameter in determining the overall reaction rate. The graphical trend of reaction rate for experimental and predicted results should be similar. An explanation for the deviations observed was due to the SCM model assumptions that were made upon developing the kinetic model. Those assumptions were that the porosity and pellet size of sample was constant during the reduction.

Firstly, the sample was assumed to be porous without close pores for gas transport in and out during the reaction time. However, Ronald Charles Gower [15] have suggested that this situation was ideal to take place because of the presence of open and closed pores. Moreover, the porosity throughout the sample also varied and was not constant. These pores formed within the product and restricted the movement of the CH₄ gas. Therefore, until the product layer cracks to allow free movement of CH₄, the diffusion of oxygen and carbon atoms in the solid phase or gaseous reactants can only contribute to the reaction kinetics. Delay in this cracking of intermediate product layers of Ti₂O₃ also slows down the reaction. Furthermore, Ti₂O₃ does not convert directly to TiC but as another intermediate phase of TiOₓC₁₋ₓ. Studies by Dewan et al. and Guangqing Zhang et al. [5, 13] have shown that the end product to be TiOₓC₁₋ₓ instead of TiC at the reduction temperature used. The presence of these intermediates phases also was difficult to model by SCM. The slow reaction for intermediate product to transform into TiOₓC₁₋ₓ caused the build up in non-porous Ti₂O₃. As a result, mass transfer for carbon and CH₄ to penetrate the Ti₂O₃ layer was difficult.

Pure TiC was employed in developing the kinetic model instead of using the actual end product of the reaction, which was a solid solution titanium oxycarbide (TiOₓC₁₋ₓ). There was insufficient thermodynamic and physical properties for TiOₓC₁₋ₓ phases to be used for the kinetic model compared with TiC. Added to this, it was impossible to reduce titania into pure TiC at this low temperatures. Instead of producing pure TiC, a solid solution of TiOₓC₁₋ₓ with similar cubic crystalline structure as

**Figure 6.** Comparison of non-isothermal predicted and isothermal predicted with experimental reaction rate for reduction of titania at different temperatures (a) 1100°C (b) 1200°C

The comparison of temperature variation with respect to reaction rate was shown in Figure 6. From the figure, it shows the deviation between predicted and experimental measured results. On the other hand, the experimental reaction rate changed linearly with reduction time, which showed the reaction was chemically controlled. In this case, temperature was a key parameter in determining the overall reaction rate. The graphical trend of reaction rate for experimental and predicted results should be similar. An explanation for the deviations observed was due to the SCM model assumptions that were made upon developing the kinetic model. Those assumptions were that the porosity and pellet size of sample was constant during the reduction.

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TiC was produced during reduction [21]. Due to these supporting evidence, the predicted and experimental results deviation was observed. Even though there were deviations between the predicted and experimental results, the model still shows the kinetic trends that was expected from SCM. The trend indicated the increasing in rate and extent of reduction when temperature increases when governed by chemically controlled reaction rate.

6. Conclusions
Titania was reduced to TiO$_x$C$_{1-x}$ in a temperature range of 1100 - 1200°C by liquefied petroleum gas (LPG)-hydrogen-argon gas mixtures. The variation in the LPG flowing time and reduction time showed a significant effect on the extent of reduction. The results obtained confirmed that the reduction rate was accelerated by the longer flow time of LPG. The highest experimental extent of reduction of about 37.9% occurred at a temperature of 1200°C with 3 hours reduction time and 20 min of LPG flowing time. The reduction rates increased with increasing reduction temperature and LPG flowing time. The SCM was implemented in MATLAB that modelled isothermal and nonisothermal reduction. For the nonisothermal reduction at 1200°C at 3 hours with 20 min of LPG flowing time, the R’ calculated by the kinetic model was about 82%. There were differences between the predicted and experimental results, but the overall kinetic trend of reduction rate was similar. The differences was due to limitation of SCM to predict changes in porosity, thermodynamic properties of TiO$_x$C$_{1-x}$ and minute changes in temperature in the concentric shells during reduction. Future models will address this limitations.

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Nomenclature

| Symbol | Description |
|--------|-------------|
| A      | reactant solid |
| B      | reactant gas |
| C      | product solid |
| CP_A   | Heat capacity of gas reactant (calorie/mole.°K) |
| CP_B   | Heat capacity of gas product (calorie/ mole.°K) |
| D      | product gas |
| Eq.    | Equation |
| G      | mass flow rate (gram/cm$^2$.sec) |
| K_eq   | Equilibrium constant |
| R'     | Percent of reduction |
| R_o    | Initial radius (cm) |
| R      | Final radius (cm) |
| T_g    | Gas temperature (°K) |
| T_o    | Initial temperature (°K) |
| T_s    | Surface pellet temperature |
| atm    | Atmosphere |
| d_o    | Sphere diameter |
| r_i    | Position of reaction interface (cm) |
| t      | time |
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