**Biochemical Sciences**  
**Hydrogenation of CO on cobalt catalyst in Fischer-Tropsch Synthesis**  
--Manuscript Draft--

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<th>Manuscript Number:</th>
<th>BIOCHEM-11-105</th>
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<td><strong>Full Title:</strong></td>
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</tr>
<tr>
<td><strong>Short Title:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Article Type:</strong></td>
<td>Research Article</td>
</tr>
<tr>
<td><strong>Section/Category:</strong></td>
<td>Journal of Thermodynamics &amp; Catalysis</td>
</tr>
<tr>
<td><strong>Keywords:</strong></td>
<td>Fischer-Tropsch Synthesis, Fixed-bed Reactor, Co/K/Al2O3 Catalyst, Kinetic Modeling</td>
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<tr>
<td><strong>Corresponding Author:</strong></td>
<td>H. Atashi, IRAN (ISLAMIC REPUBLIC OF)</td>
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<tr>
<td><strong>First Author:</strong></td>
<td>H. Atashi</td>
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**Suggested Reviewers:**

**Opposed Reviewers:**
Hydrogenation of CO on cobalt catalyst in Fischer–Tropsch Synthesis

H. Atashi¹,*, M. Mansouri¹, A. A. Mirzaei², and M. Karimi¹

¹ Department of Chemical Engineering, University of Sistan & Baluchestan, Zahedan 98164-161, Iran
² Department of Chemistry, University of Sistan & Baluchestan, Zahedan 98164-161, Iran
*Email: atashi.usb@gmail.com

Abstract

The kinetic experiments of Fischer–Tropsch synthesis (FTS) over an industrial Co/K catalyst are carried out in a micro-fixed-bed reactor under the conditions as follows: temperature of 483–513 K, pressure of 8 bar, H₂/CO feed ratio of 1–3, and space velocity of 2700–5200 h⁻¹. The optimal amount of catalyst containing 15wt.%Co/10wt.%K/Al₂O₃ was prepared using impregnation procedure. The combined enol/carbide mechanism as the rate-controlling step gives the most plausible kinetic model among the nine different models tested. The activation energies for optimal kinetic model and power law equation were obtained 111.5 kJ/mol and 100 kJ/mol, respectively.

Key words: Fischer–Tropsch Synthesis, Fixed-bed Reactor, Co/K/Al₂O₃ Catalyst, Kinetic Modeling

Introduction

The process of converting the synthesis gas into liquid fuels (FTS) is a well-known technology. This method is a promising, developing option for environmentally sound
production of chemicals and fuels from coal and natural gas. In view of large coal and natural
gas reserves and dwindling petroleum reserves worldwide, it is projected to play an ever
increasing role in the coming decades [1, 2].

Cobalt-based catalysts are the preferred catalysts for hydrocarbon synthesis because of
their high FTS activity, selectivity for long-chain paraffins, and low activity for the water–gas
shift reaction [3]. The kinetics of FTS on cobalt catalysts has received significant attention; in
fact, several previous studies [4-8] report kinetic data and rate expressions. Reaction orders
for H₂ and CO are in the range 0.5 to 2 and −1.0 to +0.65, respectively; activation energies
from these studies cover a range 98–103 kJ/mol [8].

The mechanistic kinetic rate expressions for cobalt catalysts are based on the formation of
the monomer species as the rate-determining step in the consumption of synthesis gas. Many
kinetic equations have been proposed in the literature for various cobalt catalysts, and these
have been obtained either empirically (using a power-law rate equation) or to fit a proposed
mechanism [6-9].

Our objective is to develop intrinsic rate expressions for the CO conversion to Fischer–
Tropsch products over an impregnation cobalt catalyst on the basis of realistic mechanisms.
The kinetics of FT reaction was studied and the rate expressions were tested against
experimental data that was obtained on the selected catalysts. A model was successfully
devised and the kinetics parameters were determined. Also, a power law kinetic equation for
the carbon monoxide rate was obtained.
EXPERIMENTAL

Catalyst preparation

The optimal amount of 15wt.%Co/10wt.%K/Al$_2$O$_3$ was prepared by impregnation with an aqueous solutions of Co(NO$_3$)$_2$·6H$_2$O and KNO$_3$ to incipient wetness of γ-Al$_2$O$_3$, which had been previously calcined at 400°C for 8 h to remove the surface adsorbed impurities (BET surface area of 217 m$^2$/g, pore volume of 0.7 cm$^3$/g). The impregnated sample was dried at 110°C for 2 h and calcined in air at 400°C for 8 h (heating rate of 10°C between 110 and 400°C); the calcined catalyst was reduced in situ (in the fixed bed reactor described below) in pure H$_2$ at 400°C for 16 h (heating rate of 10°C between 25 and 400°C).

Fixed bed reactor system

FTS was carried out in a fixed-bed micro-reactor made of stainless steel with an inner diameter of 12 mm. Three mass flow controllers (Brooks, Model, 5850E) were used to adjust automatically flow rate of the inlet gases comprising CO, H$_2$ and N$_2$ (purity of 99.999%). Mixture of CO, H$_2$ and N$_2$ was subsequently introduced into the reactor, which was placed inside a tubular furnace (Atbin, Model ATU 150-15). Temperature of the reaction was controlled by a thermocouple inserted into the catalytic bed and visually monitored by a computer. The catalyst was in situ pre-reduced at atmospheric pressure under H$_2$–N$_2$ flow (N$_2$/H$_2$ = 1, flow rate of each gas = 30 ml/min), at 400°C for 16 h. In each test, 1.0 g catalyst was loaded and the reactor operated about 12 h to ensure steady state operations were attained.

Catalytic evaluation

Experiments were conducted with mixtures of H$_2$, CO and nitrogen in a temperature range from 210 to 240°C, H$_2$/CO feed ratios of 1/1-3/1 (mol/mol) at the pressure of 8 bar. The
arrangements of the parameters and the related levels are shown in Table 1. In all of the experiments, the space velocities were between 2700 and 5200 h$^{-1}$.

To avoid the effect of deactivation, fresh catalysts were loaded in each experiment. To achieve the isothermal conditions in a catalytic bed, the catalyst was diluted with an inert material (quartz). Axial temperature distribution was ensured using Mear’s [10, 11] criterion, that is with $L/d_p > 50$. Also, plug-flow was assumed for the gaseous feed. The experimental reaction rate was determined as follows:

$$Rate\ of\ conversion\ of\ CO = \frac{\text{(fractional conversion)} \times \text{(input flow rate of CO)}}{\text{weight of the catalyst}} \quad (1)$$

Theory

Kinetic expressions

In order to derive rate equations to be adjusted with the data in Table 1, we used LHHW theory to obtain kinetic models. According to this theory, a reaction mechanism should be adopted. Two key assumptions of this theory are: (1) Attraction heats are constant, (2) Inherent reaction rates are proportional to surface covers of reactors. To simplify the kinetic models, following assumptions are taken into consideration [12, 13]: (1) Presence of an irreversible controlling stage, although all of the other stages are considered to be near the thermodynamic equilibrium. (2) Concentrations of all of the mediums on the catalyst surface are in steady state. (3) Catalytic locations are steady and distributed homogenously. (4) Through the whole temperature and pressure region, rate controller stage and the most abundant surface medium are remained unchanged. (5) Elementary attraction of hydrogen and carbon monoxide in pseudo-equilibrium state are within concentrations of gaseous phase. (6) Water is removed after the CO decomposition irreversibly.
Statistical Criteria using Polymath Software

Least square method and non-linear regression analysis based on the summarized values in Table 1 is used to determine the power-law equation parameters and kinetic model parameters from experimental data provided in Table 2 using polymath® software. The software uses Levenberg–Marquardt algorithm to estimate the constants of the model. There are some conditions to find the best model[14]: (1) Obtained constants must be positive. (2) Optimal model or equation is the one which gives the reliable $R^2$. (3) Coefficients of the equation must obey Arrhenius and Vanthouff rules. (4) The equation must have the ability to predict the behavior of a differential reactor. A good equation can satisfy all of the mentioned rules. Different Statistical indices in Polymath software can be used to determine the quality of regression models and compare them.

RESULTS AND DISCUSSION

Development of Kinetic Equations

Considering the proceeding assumptions, three mechanisms were offered on the basis of various monomer formation (elementary reactions) and carbon chain distribution pathways. An elementary reactions set on sites for each model is summarized in Table 2.

To derive each kinetic model, initially one of the elementary reaction (in some case two or three) steps was assumed as rate-determining step and all other steps were considered at equilibrium. Then, all of the models obtained were fitted separately against the experimental data. In the interest of conciseness, only certain selected kinetic models are reported in the Table 3.

For example derivation of the rate equation for FT-I4 is explained here. To do this, the first step is considered to be the rate limiting stage and the reaction is irreversible. The remaining steps can be considered to be quick and at equilibrium.
The rate expression of the rate-determining step for FT-I4 model where surface carbon reacts with adsorbed dissociated hydrogen as the rate limiting step, can be expressed irreversible adsorption as follows:

\[-r_{CO} = k_4 \theta_C \theta_H = k_6 \theta_O \theta_H\]  

where \(-r_{CO}\) is the rate of disappearance of CO, \(k_4\) and \(k_6\) are the forward rate constant for elementary reaction of numbers of 4 and 6 respectively, and \(\theta_i\) is the surface fraction occupied with adsorbed species \(i\). The fraction of vacant sites, \(\theta_S\), can be calculated from the following balance equation:

\[\theta_S + \theta_{CO} + \theta_H + \theta_{H,CO} + \theta_{CH_2} + \theta_O + \theta_{OH} + \theta_{H,CO} = 1\]  

In this case, it is assumed that adsorbed dissociated hydrogen and surface carbon occupies a significant fraction of the total numbers of sites. Other species were assumed to be negligible in the stoichiometric balance:

\[\theta_S + \theta_C + \theta_H = 1\]  

The surface coverage of carbon monoxide and adsorbed dissociated hydrogen are calculated from the site balance, and the preceding reaction steps which are at quasi-equilibrium:

\[CO + S \rightleftharpoons \overset{k_1}{\underset{k_{1,des}}{\longleftrightarrow}} COs\]  

\[k_1 P_{CO} \theta_S - k_{1,des} \theta_{CO} = 0\]  

\[\theta_{CO} = K_1 P_{CO} \theta_S\]  

\[K_1 = \frac{k_1}{k_{1,des}}\]  

where \(K_1\) is the equilibrium constant of CO adsorption step. Thus, if the next stages are assumed to be near the thermodynamic equilibrium, available surface ratios can be determined using partial pressures of reactors.
\[ \theta_H = K_3^{1/2} P_{H_2}^{1/2} \theta_S \]  
(8)

\[ \theta_O = \frac{k_4}{k_6} \theta_C \]  
(9)

\[ \theta_C = \frac{K_2 \theta_{CO} \theta_S}{\theta_O} \]  
(10)

Substituting equation (7) and then (9) in equation (10) gives:

\[ \theta_C = \frac{K_2 \theta_{CO} \theta_S}{\theta_O} = \left( \frac{K_1 K_2 k_6}{k_4} \right)^{1/2} P_{CO}^{1/2} \theta_S \]  
(11)

Substituting Equation (8) and (11) into Equation (4), the ratio of free active site can be expressed as:

\[ \theta_S = \frac{1}{1 + \left( \frac{K_1 K_2 k_6}{k_4} \right)^{1/2} P_{CO}^{1/2} + K_3^{1/2} P_{H_2}^{1/2}} \]  
(12)

Substitution of the fraction of vacant sites in Equation (2), the final rate expression is obtained as:

\[ -r_{CO} = \frac{(k_4 k_6 K_1 K_2 K_3)^{1/2} P_{CO}^{1/2} P_{H_2}}{(1 + \left( \frac{K_1 K_2 k_6}{k_4} \right)^{1/2} P_{CO}^{1/2} + K_3^{1/2} P_{H_2}^{1/2})^2} = \frac{k P_{CO}^{1/2} P_{H_2}}{(1 + a P_{CO}^{1/2} + b P_{H_2}^{1/2})^3} \]  
(13)

Table 3 summarizes the final form of the different rate expressions for the 9 possible kinetic models considered, whereas Table 4 shows the kinetic and adsorption parameters for the several kinetic models. It can be seen that the pressure dependency of CO and H2 in the numerator ranges from 1/2 to 1, and 1/2 to 2, respectively. The denominator is quadratic in case of a dual site elementary reaction, in contrast to a single site rate-determining step. The denominator consists of the individual contributions of significantly plentiful species on the catalyst surface.

Also, power law kinetic equation for the carbon monoxide rate was considered for comparison with experimental data. Yang et al. [5] obtained empirical rate expressions for
supported cobalt catalysts using a fixed-bed reactor via regression of a power-law equation of
the general form:

\[-r_{CO} = k_0 \exp\left(-\frac{E}{RT}\right)P_{CO}^m P_{H_2}^n\]  \hspace{1cm} (14)

where \(P_{CO}\) the partial pressure of carbon monoxide, \(k_0\) the reaction rate constant, \(E\) the
activation energy of CO consumption, \(m\) the reaction order for CO, and \(n\) the reaction order
for \(H_2\).

**Model parameters and model discrimination**

CO consumption rate was obtained from the data in Table 1 by using the differential
method of data analysis. The kinetic data presented in Table 1 for CO conversion were used
for testing the power law equation and nine models listed in Table 3. Before inserting the
equations in the polymath® software, Arrhenius and adsorption equations were substituted in
kinetics models: Equation (15) and (16) were substituted for \(k\) and \(a\), respectively.

\[k = k_0 \exp\left(-\frac{E}{RT}\right)\]  \hspace{1cm} (15)

\[a = a_0 \exp\left(\frac{\Delta H}{RT}\right)\]  \hspace{1cm} (16)

According to the statistical results obtained by inserting the data and models, the best
model can be selected. Based on the kinetic data, the only plausible mechanism was found to
be the FT-III model with combined enol/carbide mechanism as the rate-controlling step.
Based on statistical information, the best model is found to be FT-III2 that has the less
deviation from experimental data. Therefore there are best fitted by a LHHW approach rate
form \(-r_{CO} = k_2 K_1 P_{CO} P_{H_2}/(1 + K_1 P_{CO})\), where activation energy is obtained to be 111.5 kJ/mol.
The other models are ignored because: (1) calculations of partial regression related to kinetic equation exceed the maximum number of iterations or trial and errors, (2) confidence interval parameter is high when compared with its absolute values, (3) their constants are negative, (4) do not give the responsible $R^2$.

The data of this study are fitted fairly well by a power law equation in the form

$$-r_{\text{CO}} = 2.1 \times 10^8 \exp\left(\frac{-1 \times 10^5}{RT}\right) \frac{P_{\text{CO}}^{-0.45}}{P_{\text{H}_2}^{0.85}}.$$  

The $R^2$ value has been obtained 0.99, which shows power law equation is well matched with the experimental data. Table 5 shows the kinetic parameters calculated for the kinetic FT-IV2 model and power law equation.

### Conclusion

The optimal amount of catalyst containing 15wt.%Co/10wt.%K/Al$_2$O$_3$ was prepared using impregnation procedure. Experiments for the kinetics of the hydrocarbon formation over an cobalt catalyst were obtained over a wide range of industrially relevant reaction conditions. The data of this study are best fitted by the simple LHHW approach rate of the form

$$-r_{\text{CO}} = \frac{k P_{\text{CO}} P_{\text{H}_2}}{1 + a P_{\text{CO}}}.$$  

The values of kinetic constants were obtained and the activation energy was found to be 111.5 kJ/mol for the best model. The data are fitted fairly well by a power law equation in the form of

$$-r_{\text{CO}} = 2.1 \times 10^8 \exp\left(\frac{-1 \times 10^5}{RT}\right) P_{\text{CO}}^{-0.45} P_{\text{H}_2}^{0.85}.$$  

### References


Tables

**Table 1.** Summary of experimental conditions and results at P = 8 bar and T = 210–240°C.

<table>
<thead>
<tr>
<th>Number of data</th>
<th>Temperature (K)</th>
<th>X_{CO} (%)</th>
<th>P_{CO} (bar)</th>
<th>F/W (mol/gr cat. h)</th>
<th>\text{-}r_{CO} (mmol/gr cat. h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>483.15</td>
<td>2.6</td>
<td>2.81</td>
<td>1.95</td>
<td>0.172</td>
</tr>
<tr>
<td>2</td>
<td>483.15</td>
<td>3.2</td>
<td>2.35</td>
<td>2.90</td>
<td>0.173</td>
</tr>
<tr>
<td>3</td>
<td>483.15</td>
<td>3.6</td>
<td>3.55</td>
<td>1.93</td>
<td>0.154</td>
</tr>
<tr>
<td>4</td>
<td>483.15</td>
<td>4.8</td>
<td>2.25</td>
<td>3.81</td>
<td>0.139</td>
</tr>
<tr>
<td>5</td>
<td>493.15</td>
<td>3.2</td>
<td>3.05</td>
<td>1.94</td>
<td>0.289</td>
</tr>
<tr>
<td>6</td>
<td>493.15</td>
<td>2.4</td>
<td>1.41</td>
<td>1.95</td>
<td>0.195</td>
</tr>
<tr>
<td>7</td>
<td>493.15</td>
<td>5.3</td>
<td>3.33</td>
<td>2.84</td>
<td>0.287</td>
</tr>
<tr>
<td>8</td>
<td>493.15</td>
<td>2.8</td>
<td>2.59</td>
<td>0.97</td>
<td>0.143</td>
</tr>
<tr>
<td>9</td>
<td>503.15</td>
<td>5.1</td>
<td>1.81</td>
<td>1.90</td>
<td>0.186</td>
</tr>
<tr>
<td>10</td>
<td>503.15</td>
<td>7.9</td>
<td>4.73</td>
<td>1.84</td>
<td>0.355</td>
</tr>
<tr>
<td>11</td>
<td>503.15</td>
<td>5.5</td>
<td>3.61</td>
<td>1.42</td>
<td>0.272</td>
</tr>
<tr>
<td>12</td>
<td>503.15</td>
<td>6.7</td>
<td>2.23</td>
<td>2.80</td>
<td>0.286</td>
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<tr>
<td>13</td>
<td>513.15</td>
<td>8.8</td>
<td>2.88</td>
<td>3.65</td>
<td>0.698</td>
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<tr>
<td>14</td>
<td>513.15</td>
<td>7.6</td>
<td>3.63</td>
<td>2.31</td>
<td>0.650</td>
</tr>
<tr>
<td>15</td>
<td>513.15</td>
<td>7.1</td>
<td>3.41</td>
<td>1.86</td>
<td>0.520</td>
</tr>
<tr>
<td>16</td>
<td>513.15</td>
<td>8.6</td>
<td>4.58</td>
<td>2.29</td>
<td>0.712</td>
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**Table 2.** Elementary reactions mechanism set for FTS.

<table>
<thead>
<tr>
<th>Model</th>
<th>Number</th>
<th>Elementary Reaction</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>CO + s ↔ COs</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>COs + s ↔ Cs + Os</td>
<td></td>
</tr>
<tr>
<td>FT-I</td>
<td>H2 + 2s ↔ 2Hs</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cs + Hs ↔ CHs + s</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CHs + Hs ↔ CH2s + s</td>
<td></td>
</tr>
</tbody>
</table>
Os + Hs → HOs + s
HOs + Hs → H₂Os
H₂O + s → H₂Os

CO + s ↔ COs
H₂ + 2s ↔ 2Hs
COs + Hs ↔ HCOs + s
HCOs + Hs ↔ Cs + H₂Os
Cs + Hs ↔ CHs + s
CHs + Hs ↔ CH + s + s
H₂O + s → H₂Os

FT-II

FT-III

Table 3. Reaction rate expressions for the FTS, \( r_{FT} \) (mmol \( g_{cat}^{-1} h^{-1} \))

<table>
<thead>
<tr>
<th>Model of rate controlling</th>
<th>Kinetic equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-I1</td>
<td>( kp_{CO} / (1 + aP_{CO}^{1/2} + bP_{H_2}^{1/2}) )</td>
</tr>
<tr>
<td>FT-I3</td>
<td>( kp_{H_2} / (1 + aP_{CO}^{1/2} + bP_{H_2}^{1/2})^2 )</td>
</tr>
<tr>
<td>FT-I4</td>
<td>( kp_{CO}^{1/2}P_{H_2}^{1/2} / (1 + aP_{CO}^{1/2} + bP_{H_2}^{1/2})^2 )</td>
</tr>
<tr>
<td>FT-I5</td>
<td>( kp_{CO}^{3/4}P_{H_2}^{3/4} / (1 + aP_{CO}^{1/2}P_{H_2}^{-1/4} + bP_{H_2}^{1/2})^2 )</td>
</tr>
<tr>
<td>FT-II1</td>
<td>( kp_{CO} / (1 + aP_{CO}^{1/2}) )</td>
</tr>
<tr>
<td>FT-II3</td>
<td>( kp_{CO}^{1/2}P_{H_2} / (1 + aP_{CO}^{1/2}) )</td>
</tr>
<tr>
<td>FT-III1</td>
<td>( kp_{CO} / (1 + aP_{CO}) )</td>
</tr>
<tr>
<td>FT-III2</td>
<td>( kp_{CO}P_{H_2}^2 / (1 + aP_{CO}) )</td>
</tr>
<tr>
<td>FT-III3</td>
<td>( kp_{CO}P_{H_2}^2 / (1 + aP_{CO}) )</td>
</tr>
</tbody>
</table>

Table 4. Parameters for the FT kinetic models

<table>
<thead>
<tr>
<th>Model of rate controlling</th>
<th>( k(x) ) (mmol g⁻¹ h⁻¹ bar⁻²)</th>
<th>( a(x) ) (bar⁻²)</th>
<th>( b(x) ) (bar⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-I1</td>
<td>( k_1(-1) )</td>
<td>( (k_d K_3 K_2 / k_d)^{1/2} (-1/2) )</td>
<td>( K_3^{1/4} (-1/2) )</td>
</tr>
<tr>
<td>FT-I3</td>
<td>( k_3(-1) )</td>
<td>( (k_d K_3 K_2 / k_d)^{1/2} (-1/2) )</td>
<td>( K_3^{1/4} (-1/2) )</td>
</tr>
</tbody>
</table>
Table 5. Values of the kinetic parameters, activation energy and heat of adsorption of CO with various equations.

<table>
<thead>
<tr>
<th>Equation</th>
<th>( k_0 \text{ (mol g}^{-1}\text{Cat h}^{-1}\text{bar}^{-1}) )</th>
<th>( E \text{ (kJ/mol)} )</th>
<th>( a_0 \text{ (bar}^{0.5} )</th>
<th>( \Delta H \text{ (kJ/mol)} )</th>
<th>( m(-) )</th>
<th>( n(-) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-I4</td>
<td>( (k_6K_4K_2K_3) )</td>
<td>( (k_4K_2/k_6) )</td>
<td>( K_3^{1/4} )</td>
<td>( -1/2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT-I5</td>
<td>( (k_8K_4K_2K_3) )</td>
<td>( K_3^{1/4} )</td>
<td>( (k_4K_2/k_6) )</td>
<td>( K_3^{1/4} )</td>
<td>( -1/2 )</td>
<td></td>
</tr>
<tr>
<td>FT-III1</td>
<td>( k_1 )</td>
<td>( -1 )</td>
<td>( K_1 )</td>
<td>( -1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT-III2</td>
<td>( k_2K_1 )</td>
<td>( -2 )</td>
<td>( K_1 )</td>
<td>( -1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT-III3</td>
<td>( k_2K_1K_2 )</td>
<td>( -3 )</td>
<td>( K_1 )</td>
<td>( -1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a FT-III2</td>
<td>( 1.01 \times 10^{11} )</td>
<td>111.5</td>
<td>163.2</td>
<td>-5.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b Power law</td>
<td>( 2.1 \times 10^8 )</td>
<td>100</td>
<td></td>
<td>-0.45</td>
<td>0.85</td>
<td></td>
</tr>
</tbody>
</table>

\( a = -2, b = -0.4 \)