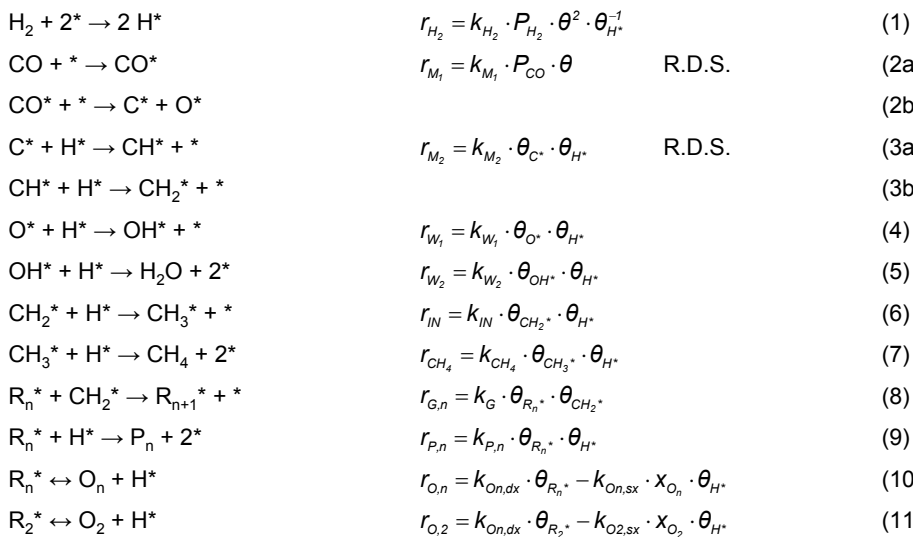


## Introduction:

A global kinetic model of the FTS over a state-of-the-art Co/Al<sub>2</sub>O<sub>3</sub> catalyst is developed in a fixed bed micro-reactor under conditions relevant to industrial operation (temperature, 210-235°C; pressure, 8-25 bar; H<sub>2</sub>/CO feed molar ratio, 1.8-2.7; gas hourly space velocity, 2000-7000 cm<sup>3</sup>(STP)/h/g<sub>catalyst</sub>). On the basis of proposed reaction mechanisms, developed according to the carbide theory and the alkyl mechanism, rate expressions for n-paraffins and α-olefins formation are derived.

## Results:

The following comprehensive FTS kinetic scheme (and the related rate equations), developed on the basis of a reaction mechanism resulting from literature analysis and from chemical enrichment experiments and composed by elementary reactions, are adopted in this work:



### Assumptions:

- Rate constants involved in eq. 8-10 are independent of n.
- A specificity was assumed in the kinetic constants involved in eqs. 7, 11 (CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> formation, respectively).
- The reactor temperature affects the CO conversion, but not the product selectivity: activation energies introduced only for the steps involved in the monomer formation.

Table 1: Estimates of the kinetic parameters

parameter	value	unit
$K_{\text{H}_2}$	$3.38 \times 10^{-4}$	mmol s <sup>-1</sup> g <sup>-1</sup> bar
$E_{\text{H}_2}$	442.42	kJ mol <sup>-1</sup>
$K_{\text{M}_1}$	$2.76 \times 10^{-3}$	mmol s <sup>-1</sup> g <sup>-1</sup> bar
$E_{\text{M}_1}$	231.94	kJ mol <sup>-1</sup>
$K_{\text{M}_2}$	$5.81 \times 10^1$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{W}_1}$	$2.39 \times 10^4$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{W}_2}$	$1.06 \times 10^7$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{IN}}$	$1.59 \times 10^1$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{CH}_4}$	$7.29 \times 10^{-2}$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{G}}$	$1.91 \times 10^1$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{P},n}$	$1.65 \times 10^2$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{O},n,dx}$	$1.99 \times 10^3$	mmol s <sup>-1</sup> g <sup>-1</sup>
$K_{\text{O},n,sx}$	$3.03 \times 10^5$	mmol s <sup>-1</sup> g <sup>-1</sup> bar
$K_{\text{O},2,sx}$	$1.06 \times 10^3$	mmol s <sup>-1</sup> g <sup>-1</sup> bar

The reactor model adopted for describing the lab-scale experimental set-up is an isothermal homogeneous plug-flow model. It is composed by 2NP+2 ordinary differential equations (eq. 12), NP+5 algebraic equations (eq. 13) and the catalytic site balance (eq. 14):

$$\frac{dF_i}{dW_{\text{cat}}} = \sum_{k=1}^{NR} \alpha_{i,k} \cdot r_k \quad \text{I.C.:} \quad W_{\text{cat}} = 0 \Rightarrow F_i = F_{i,0} \quad (12)$$

$$0 = \sum_{k=1}^{NR} \alpha_{j,k} \cdot r_k \quad (13)$$

$$\theta_{\text{tot}} = \theta + \theta_{\text{C}^*} + \theta_{\text{H}^*} + \theta_{\text{O}^*} + \theta_{\text{OH}^*} + \theta_{\text{CH}_2^*} + \sum_{n=1}^{NP} \theta_{\text{R}_n^*} \quad (14)$$

The values of the 14 adaptive parameters involved in eqs. 1-11 were estimated on the basis of a set of 46 steady state FTS runs. The regression was performed using as experimental responses the CO conversion and the selectivity to CH<sub>4</sub>, C<sub>2</sub> & C<sub>2</sub><sup>=</sup>, C<sub>3</sub> & C<sub>3</sub><sup>=</sup>, C<sub>6</sub> & C<sub>6</sub><sup>=</sup>, C<sub>10</sub> & C<sub>10</sub><sup>=</sup>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>22</sub>, C<sub>26</sub>, C<sub>30</sub>, C<sub>5+</sub> and total olefins. The estimated kinetic parameters are listed in Table 1, while Figs. 1 and 2 show the model fit of the effects of CO conversion and H<sub>2</sub>/CO feed ratio on the product distribution.

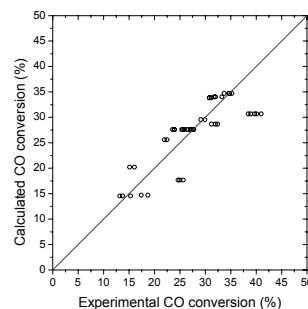


Figure 1: Parity plot for calculated and experimental CO conversion

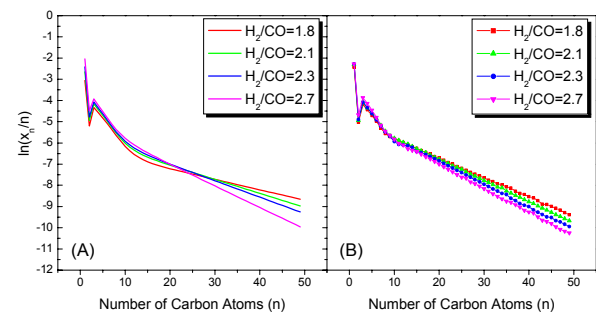


Figure 2: Effect of the H<sub>2</sub>/CO feed ratio on the product distribution: comparison between calculated (A) and experimental (B) data

## Conclusions:

For the range of industrially relevant conditions, the developed model could accurately predict both the observed CO conversion and the products distribution up to N=49, in terms of total hydrocarbons, n-paraffins and α-olefins. Accordingly it can be applied to identify optimized process conditions which are suitable to grant the desired conversion with the requested products distribution.