

# Structure-reactivity relationships in fuel stability: Experimental and kinetic modeling study of isoparaffin autoxidation

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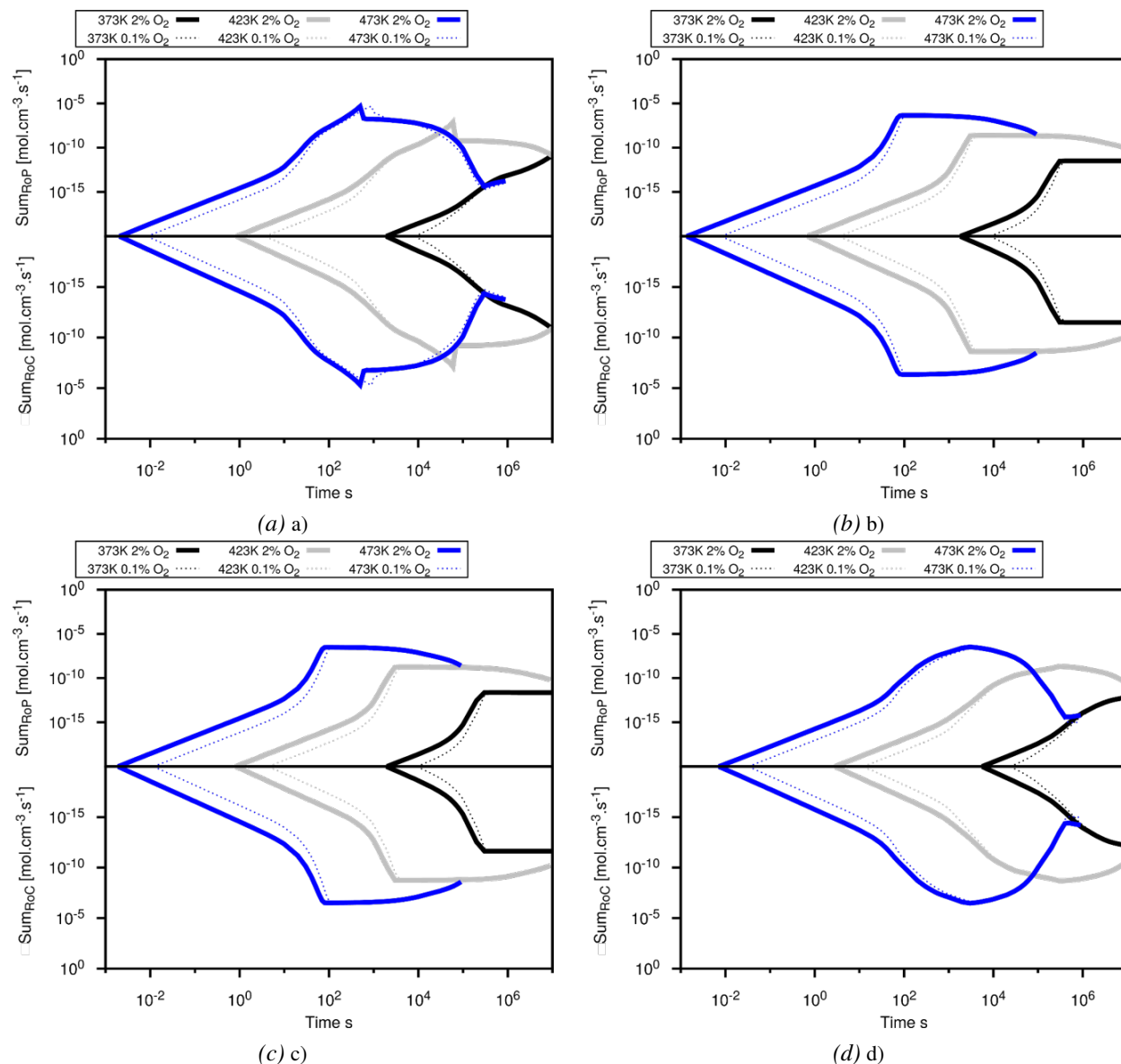
## Supplementary material

### A Complementary modeling results

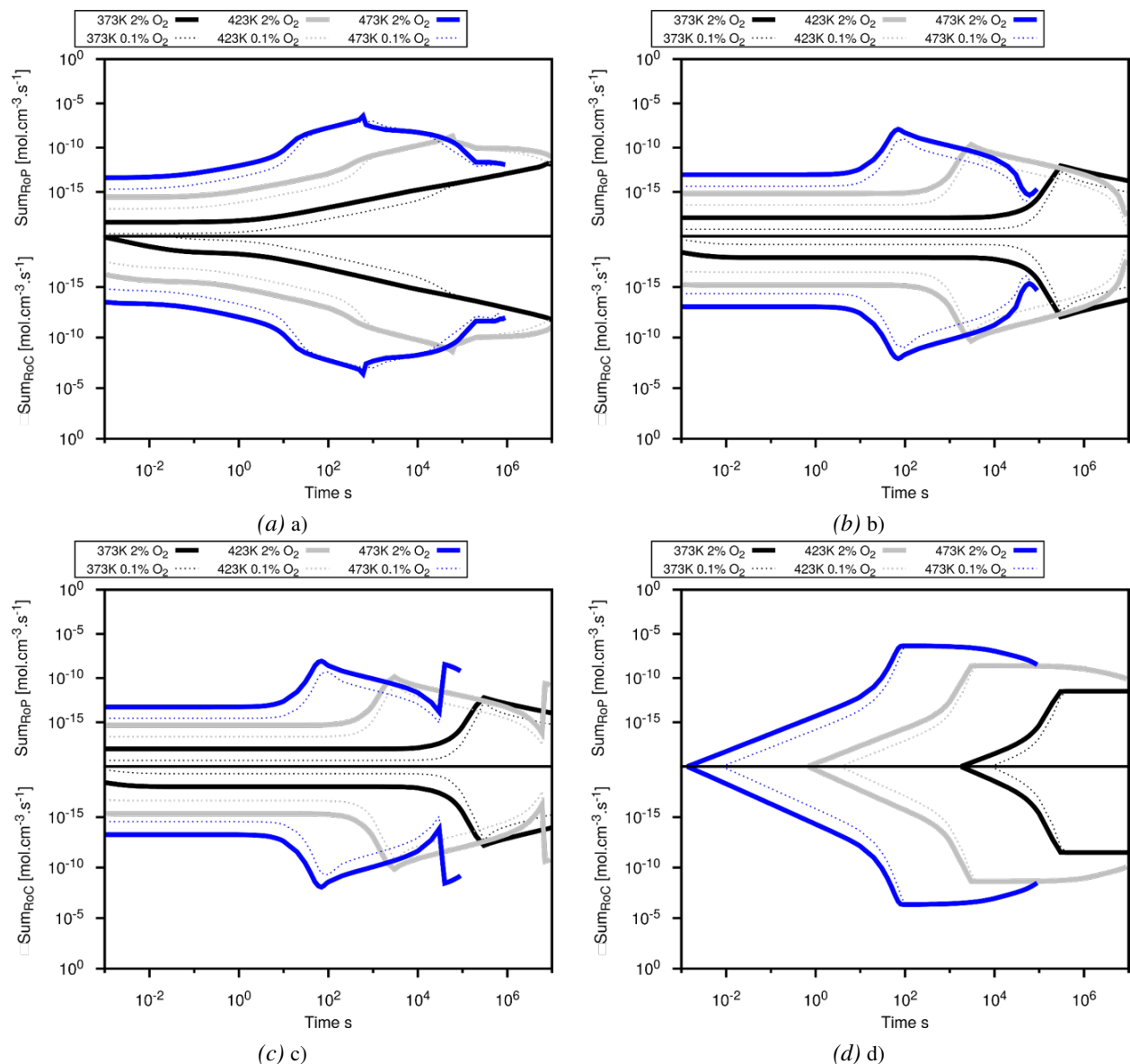
This section aims to provide additional analyses performed on the mechanisms. They are provided as supplementary materials to confirm the main conclusions of the full text and no further discussions are performed due to their limited impact on the initial conclusions.

#### A.1 Total RoC/RoP analyses

This section presents the temporal evolution of the total RoC/RoP performed on both OH and HO<sub>2</sub> radicals with the 4 mechanisms.



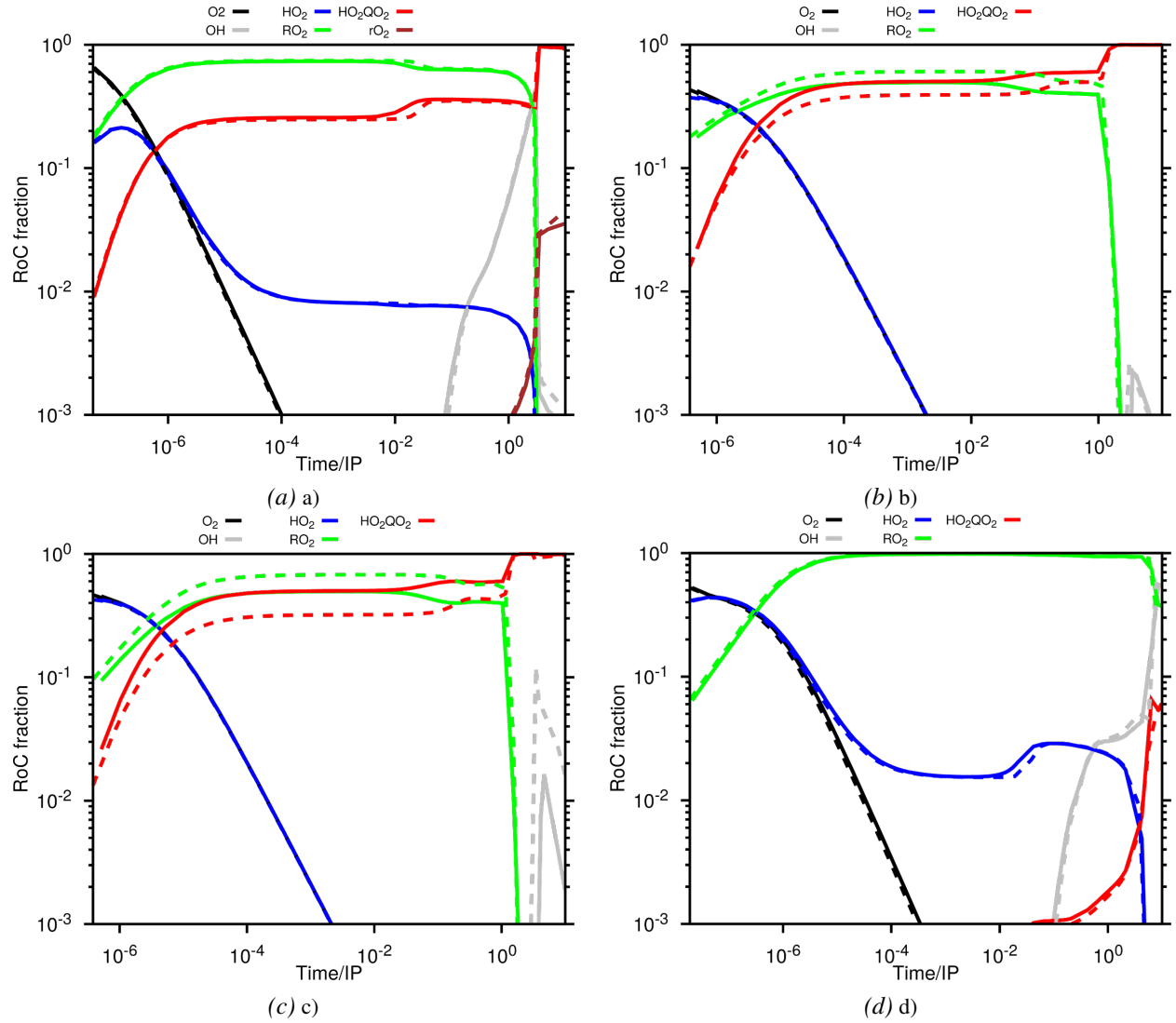
**Figure 1:** Complementary analyses presenting the total RoC/RoP of OH radicals as function of the reacting time on the four mechanisms with two oxygen concentrations and at three different temperatures. C8, MH, DMH, TMP are respectively presented on a), b), c) and d). Solid lines represent 2% oxygen concentration and dotted lines represent 1000ppm oxygen concentration.



**Figure 2:** Complementary analyses presenting the total RoC/RoP of HO2 radicals as function of the reacting time on the four mechanisms with two oxygen concentrations and at three different temperatures. C8, MH, DMH, TMP are respectively presented on a), b), c) and d). Solid lines represent 2% oxygen concentration and dotted lines represent 1000ppm oxygen concentration.

## A.2 Fuel RoC

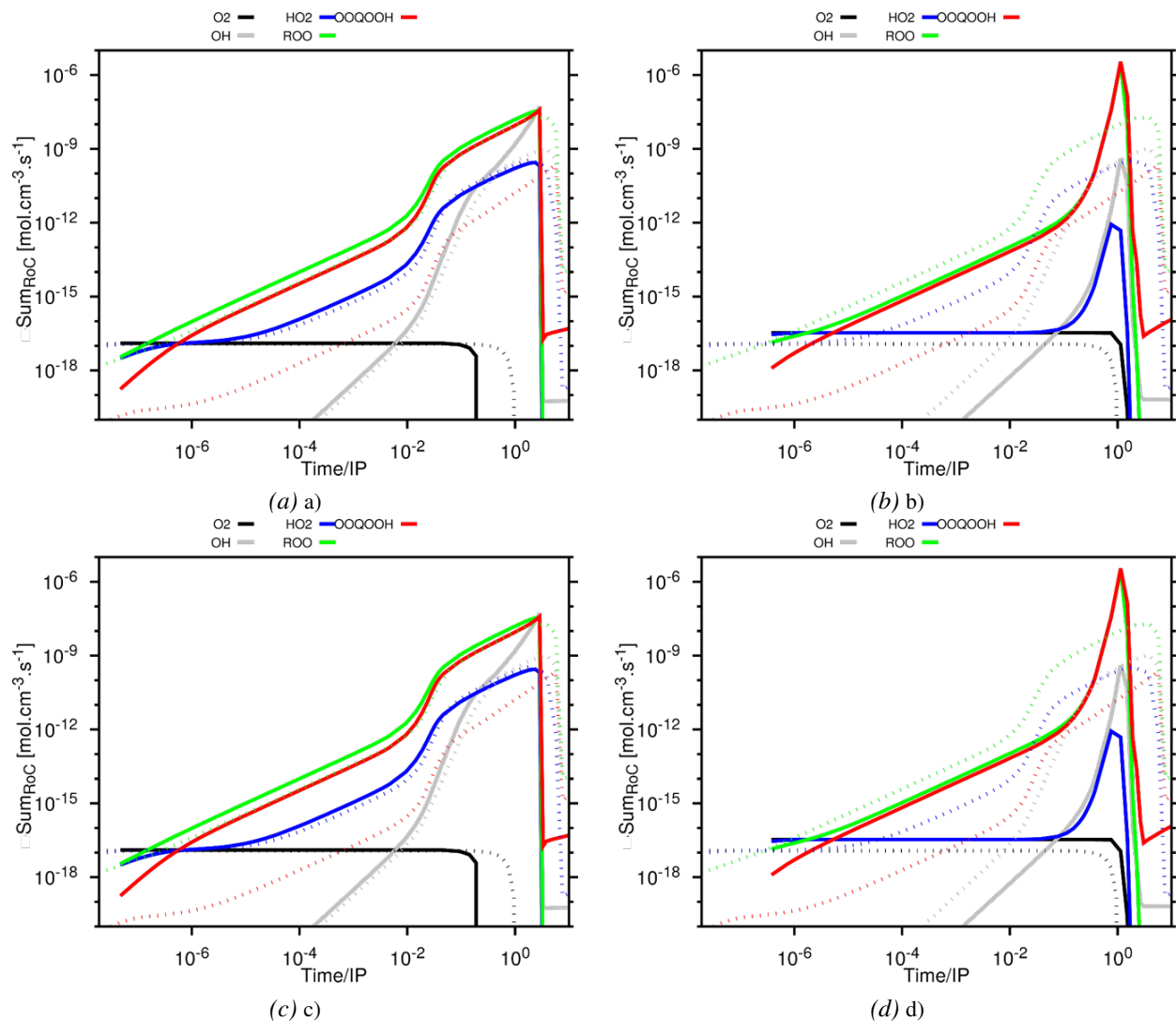
This sections aims to present the RoC analyses performed at 423K on the four mechanisms. Only the RoC of DMH presented in c) is not presented in the full text.



**Figure 3:** Effect of oxygen concentration on fuel RoC distribution on the four mechanisms: C8, MH, DMH and TMP respectively in a), b), c) and d). These analyses are conducted at 423 K with 2% and 1000 ppm of oxygen respectively in solid and dashed lines.

### A.3 Relative fuel RoC

This sections aims to present additional comparison of the temporal evolution of the fuel RoC between several pairs of mechanisms. For clarity sake, the RoC comparison between C8 and MH mechanisms, which is already presented in the article, is displayed again in a).



**Figure 4:** Temporal evolution of the sum of RoC per chemical families at 423K between several pairs of mechanisms. Figures a), b), c) and d) respectively corresponds to the comparison of C8-MH, C8-DMH, C8-TMP and MH-TMP, with the first mechanism in solid lines and the second mechanism in dotted lines.

## B Detailed presentation of the empirical structure-reactivity relationships

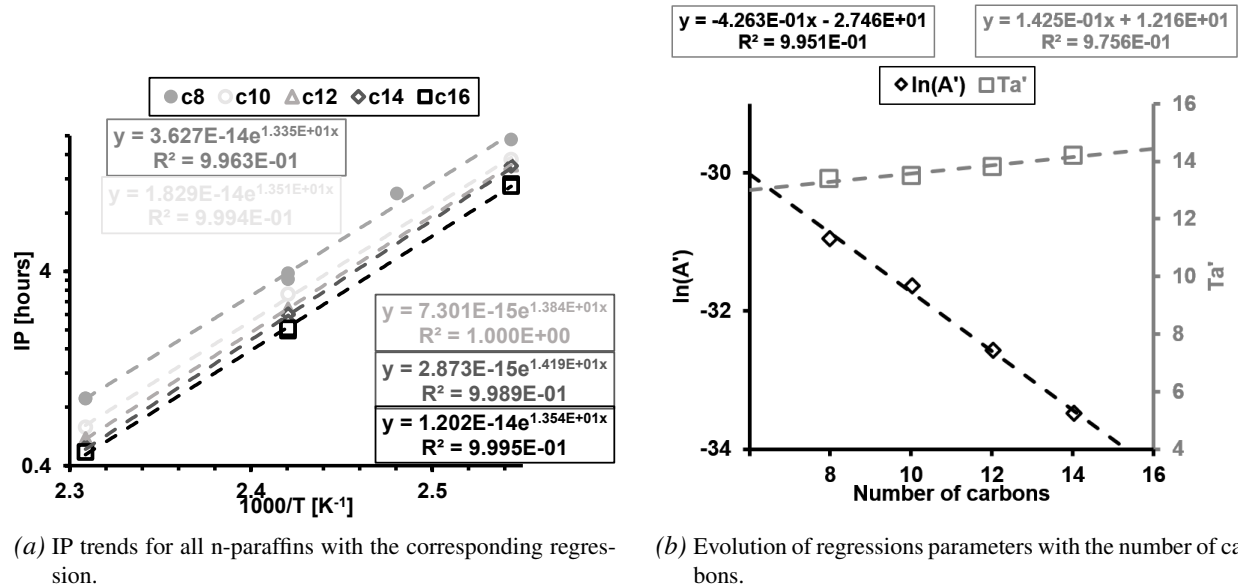
This section aims to present step by step the procedure used to establish the empirical relation presented in this article. It is established subsequently by assessing the evolution of the parameters of interest ( $A'$  and  $Ta'$ ) on n-alkane data first and then on iso-alkanes. Then an "extended empirical model" is proposed to consider both data set.

### *n-paraffins empirical model*

As concluded in literature, n-paraffins oxidability increases according to both chain length and temperature. Combining n-paraffins results from current and previous results (Chatelain et al. 2016), the n-paraffins dataset represents 21 individual Induction Period (IP) measurements between 393 and 433K<sup>1</sup>. Their stabilities can be expressed as function of an apparent kinetic rate with a  $A'$  and  $Ta'$ . The monotonic linear variation of both  $\ln(A')$  and  $Ta'$  with respect to the number of carbons, presented in Figure 5, tends to demonstrate the existence of the relation. Thus, the two expressions of  $\ln(A')$  and  $Ta'$  can be used to reconstruct  $IP_{n-para}$  as presented in Equation 1.

$$IP_{n-para,T} = A'_{n-para} \times \exp\left(\frac{Ta'_{n-para}}{T}\right)$$

With,  $\ln(A'_{n-para}) = -0.426 \times Nb_{carbons} - 27.5$  (1)  
And,  $Ta'_{n-para} = 0.1425 \times Nb_{carbons} - 12.155$



**Figure 5:** Evolution of both IPs and regression parameters as function of the number of carbons of all n-paraffins studied.

### *Iso paraffins empirical correlation*

In this section, the same approach is used to identify the evolution of  $Ta'$  and  $A'$  with the carbon types. Figure 6 illustrates the variation of those parameters across iso-alkanes with a non monotonic dependence with the number of tertiary carbons ( $Nb_{Tert.}$ ). Assuming a linear dependence of the number of quaternary

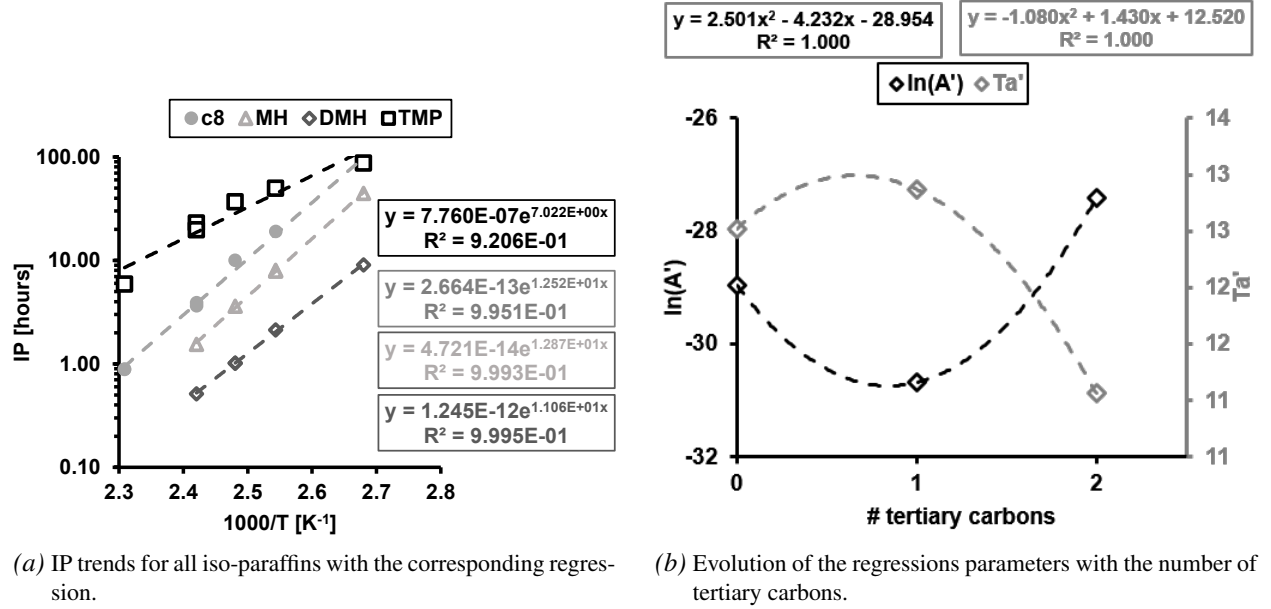
<sup>1</sup> As only one experiment is available at 373 K and only for n-octane (n-C8), this temperature range is omitted from the regression

on both  $Ta'$  and  $A'$ , a last term must be added to consider 2,2,4-trimethylpentane (TMP) results. Thus, two expressions of  $\ln(A')$  and  $Ta'$  are proposed to reconstructs  $IP_{iso-para}$  as presented in Equation 2.

$$IP_{iso-para,T} = A'_{iso-para} \times \exp\left(Ta'_{iso-para} \times \frac{1000}{T}\right)$$

With,  $\ln(A'_{iso-para}) = Nb_{Tert.} \times (2.501 \times Nb_{Tert.} - 4.232) 13.13 \times Nb_{Quat.} - 28.954$  (2)

And,  $Ta'_{iso-para} = Nb_{Tert.} \times (-1.080 \times Nb_{Tert.} 1.430) - 4.382 \times Nb_{Quat.} 12.250$



**Figure 6:** Evolution of both IPs and regression parameters as function of the number of carbons of all iso-paraffins studied.

#### Extended empirical correlation

Assuming a similar dependence of the branching, across all chain lengths, a generalized empirical correlation may be proposed for all normal/iso-paraffins compounds from Equation 2 and Equation 1. Its general expression is presented in Equation 3 with both expression of  $\ln(A')$  and  $Ta'$ . The agreement of the correlation with the two data sets are presented in Figure 7 and Figure 8. The extended correlation agreement with both Absolute Error (AE) and Relative Error (RE) according to iso/normal chemical families is summarized in Table 1. In most of conditions with IPs below 72 hours, this empirical model offers fair results ( $IP_{emp.correlation}$  20%) comparable to the sum of experimental measurements uncertainties (15%).

$$IP_{alkanes,T} = A'_{alkanes} \times \exp\left(Ta'_{alkanes} \times \frac{1000}{T}\right)$$

With,  $\ln(A'_{alkanes}) = \ln(A'_{iso-para}) 28.954 \ln(A'_{n-para})$  (3)

And,  $Ta'_{alkanes} = Ta'_{iso-para} - 12.250 Ta'_{n-para}$

While results presented here revealed a fair agreements with experimental data in most conditions. More experimental data are required to both refine and validate the empirical formula for longer branched compounds. As our dataset only contained one example with a quaternary carbon, the empirical formula should be used with caution for predictive purposes in such conditions.

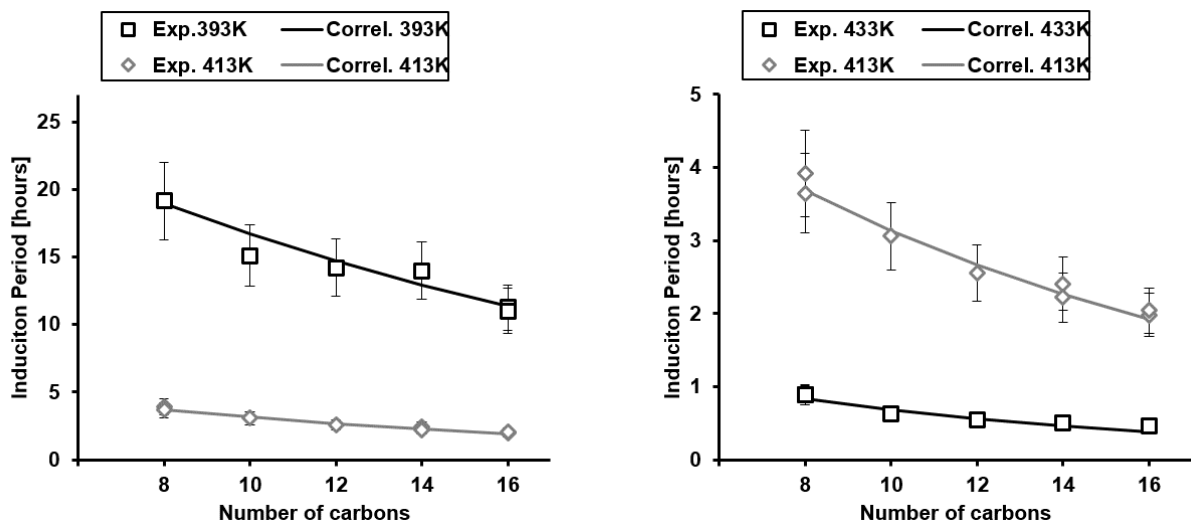


Figure 7: Validation of the extended correlation for n-paraffins chemical families

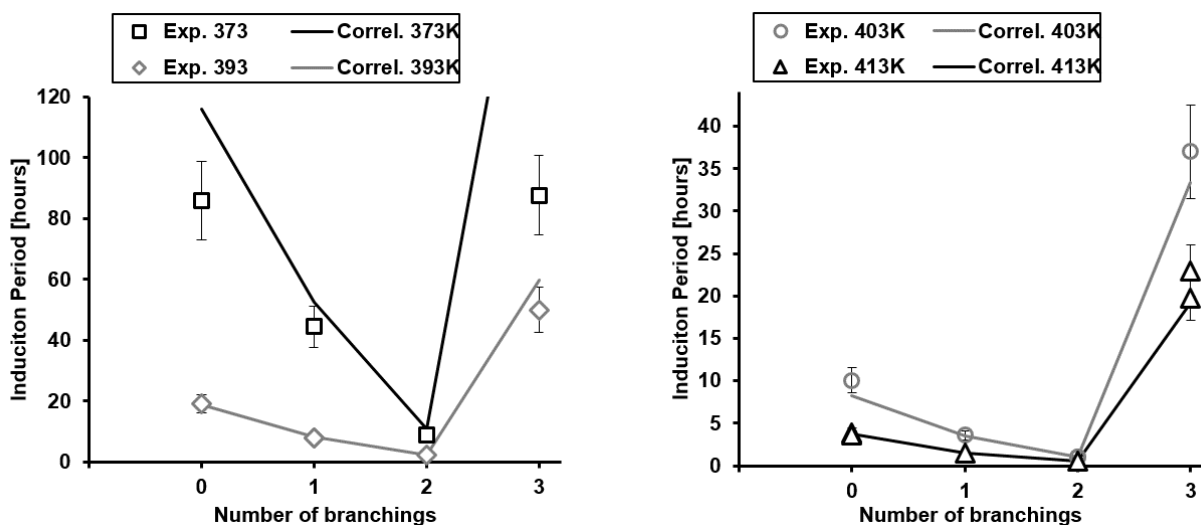


Figure 8: Validation of the extended correlation for iso-paraffins chemical families

Table 1: Performance of the extended empirical correlation according to both chemical families and IPs values

	AE values			RE values		
	Min.	Max.	Average	Min.	Max.	Average
<b>All IPs</b>						
n-paraffins	0.02	33.37	3.06	0%	60%	10%
Iso-paraffins	0.01	124.09	9.59	0%	140%	20%
<b>IPs 72h</b>						
n-paraffins	0.02	33.37	1.83	0%	60%	10%
Iso-paraffins	0.01	9.89	1.96	0%	20%	10%