A KINETIC MODELLING STUDY OF ETHANE CRACKING FOR OPTIMAL ETHYLENE YIELD

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Current generation steam cracking plants are considered to be mature. As a consequence it is becoming more and more important to know whether the underlying mechanistic cracking process offers still scope for further improvements. The fundamental kinetic limits to cracking yields have recently been researched in detail for different feed stocks with a new synthesis reactor model, *d*-RMix, incorporating a large scale mechanistic reaction scheme, SPYRO® [Dente et al., 1970; van Goethem et al., 2010]. Mathematical optimization revealed for ethane cracking a maximum ethylene yield of ~67 wt%. with a linear-concave optimal temperature profile along the reaction coordinate with a maximum temperature between 1200 and 1300 K. Further analysis of these results showed that the linear-concave shape not only suppresses the successive dehydrogenation and condensation reactions of ethylene, but mainly reduces the role of the ethane initiation reaction to form two methyl radicals.

1. INTRODUCTION

The development of the steam cracking process plant started a century ago and its understanding has evolved from an empirical description to a detailed knowledge of its fundamentals, in terms of chemical mechanism, kinetics, process requirements, design methods, etc. Van Goethem et al (2007) have given an overview of the various options for this process. The practical state-of-the-art in steam cracking plants has reached a stage of maturity in which improvements in yield and product selectivity are increasingly difficult to achieve.

For a mature process it is important to know what its fundamental limits are and whether there is still scope for further improvements. In previous work [van Goethem et al. 2010], we computationally explored the thermal and physical optimal reaction conditions for the steam cracking process to achieve maximum olefin yield. Optimal reaction conditions were derived leading to specific temperature profiles that will give the highest possible yields for four different feedstocks: ethane, naphtha, heavy naphtha and a heavy gasoil. Similar questions have been answered for the choice of flow regime and the feed distribution. Is plug flow indeed the optimal regime? Must all feed be supplied at the entrance of the reactor or should one consider multiple feed entry points along a reactor coordinate?, etc

The optimal reaction conditions for the steam cracking of ethane yielded an unconstrained solution with respect to temperature that requires a more detailed kinetic investigation. In this paper we will present and analyse the optimal reactions conditions for the steam cracking of ethane. First we will summarise the reactor synthesis model that was used in determining the optimal reactions conditions. In the following two sections the formulation of the optimization problem and the outcomes of the optimizations with different specifications for the temperature profiles are presented. Thereafter the kinetic aspects of the found results are mechanistically discussed and kinetically interpreted.

2. APPLIED REACTOR SYNTHESIS MODEL

In the synthesis of a reactor the optimal species distribution and product yield need to be determined. In view of the very short residence times and the fast reaction dynamics only steady state situations will be studied and optimised. We will use continuously distributive [van Goethem et al. 2008] species balances that describe convective transport, reactions and the injection of the feed, product removal and (macro-) mixing, the latter three functioning as distributions along a reaction volume coordinate. The steady state version is given by equation (1),a molar balance for the kth component, along reaction volume coordinate V.

$$\frac{\partial F_k(V)}{\partial V} = R_k(C,T,P) + L_j(V)F0_k - K(V)F_k(V) +$$
$$\int_0^{V_t} \left(F_k(v)M(v,V) - F_k(V)M(V,v) \right) dv \tag{1}$$

All HC have the same feed distribution function $L_j(V)$ while steam has an independent one, $j = HC$ for k ≠ H_2O and $j = H_2O$ for $k = H_2O$. Boundary condition for equation (1):

$$F0_k = \phi_m \frac{xwt_k}{Mw_k} \text{ for V=0} \tag{2}$$

Feeds weight fraction composition:

$$xwt_k = \begin{cases} \dfrac{SDR}{1+SDR} & k = H_2O \\ \dfrac{xwt_{HC,k}}{1+SDR} & else \end{cases} \quad where \sum_{\substack{k=1 \\ k \neq H_2O}}^{nComp} xwt_{HC,k} = 1 \tag{3}$$

The three distribution functions are considered along the coordinate V: the first function (L) is the feed distribution, the second function (K) for the local removal of some reaction mixture and a kernel (M) for the (macro-) mixing, forward and backward. Depending on the relative magnitude of the mixing kernel the complete spectrum between plug flow and a uniform composing by strong mixing can be achieved. The species production rates (R) are dependent on the local composition (C), temperature (T) and pressure (P). The species rate of change (R) due to the joint effect of the reactions is obtained from the SPYRO code [Dente et al., 1979; Dente et al., 1992; Dente et al., 2010], considering some 7000 reactions between some 250 species. These equations (1) form the distributive reaction-mixing model (d-RMix), which is a conceptual reactor model for process synthesis rather than real reactor equipment.

The imposed inequality constraints to temperature and pressure are: $T \leq 1300$ K and $p \geq 1$ bar, and dP/d$V \leq 0$ while the steam dilution ratio is kept fixed. The composition of the feed, its flow rate, inlet temperature and pressure are given and kept fixed. The profiles for the feed addition (L), reaction mixture removal (K), the macro-mixing kernel (M), temperature (T) and pressure (P) are free to choose within the imposed physical bounds. It is emphasized that this optimisation study aims for a temperature targeting. For that reason there is no

energy balance yet, defining the required thermal heat influx to achieve such an optimum temperature profile. The end of the reactor coordinate is free and will be used to optimize olefin yields.

3. OPTIMIZATION PROBLEM DEFINITION

The functions L, K, M and the T and P profiles in equation (1), together with the residence time need to be determined to obtain the optimal ethylene production. These functions and reaction conditions form the degrees of freedom in an NLP problem to maximise the ethylene yield, quantified here by the dry mass fraction ethylene leaving the reaction volume. The different equations, for example to relate the concentration, C, with the molar flow rate, F, are earlier reported in van Goethem et al. [2010]. To gain insight in the optimal solution we compared the optimal solution for equation (1) with two reference temperature profile solutions; see Table 1 for more details. The feed to the reaction volume of size, consisted of ethane and steam. A ratio of 0.5 is applied between steam and ethane on mass basis.

Table 1: Three optimization cases to find optimum yields with different T-profiles

Abbreviation	Description
OptPath	Optimal solution on the basis of mathematical optimization of the thermal-physical reaction problem (equation (1)) where the temperature profile is a the variable.
IsoT	For comparison purposes an optimised solution assuming a single uniform temperature with an **iso**thermal PFR, the temperature (T_{max}) value is a free variable.
TT	For comparison purposes a solution with a Typical Temperature profile as applied in cracking furnace, the maximum temperature (T_{max}) of this typical profile is the free variable.

4. OPTIMAL REACTION CONDITIONS RESULTS

The OptPath optimisation yielded the following optimal reaction condition for ethane cracking:
(a) plug flow ($M=0$) with (b) a linear-concave temperature profile $T_{OptPath}(V)$, (c) allowed isobaric pressure profile ($P=P0$) , (d) all ethane is fed at the start of the reactor ($L=0$) and (e) all effluent is collected at the end of the reactor volume ($K=0$). The upper bound on the temperature can be varied over different optimization runs. Figure 1A depicts the sensitivity of optimal ethylene yield to the maximum allowed temperature. Interestingly, compared to this optimal temperature profile (OptPath) the typical temperature profile (TT) results in only a marginally lower maximum yield (see, Figure 1A). So, current temperature profiles are suited to obtain the maximum (once through) yields for ethane cracking when cracking reactors can be build that can withstand reaction temperatures at ~1230 K. . The OptPath solution does not change with higher maximum temperature bounds and the TT solution coincide with the OptPath solution at the mentioned (maximum) temperature. The ethylene selectivity (ethylene yield divided by the ethane conversion), in the ethylene producers community also called the ultimate yield, is important because it is the net ethylene yield of a plant when all the unconverted ethane is recycled to extinction. Figure 1C shows this selectivity as a function of the maximum allowed temperatures. The maximum selectivity is obtained at the temperatures of 1145 K. This coincides with currently applied reaction conditions which are around 1145 K. However, the typical industrial ethane conversions at that temperature level of 1145 K are 70% while here the selectivity for the typical temperature (TT) profile is obtained with a conversion of 92%. So, this suggests there is still scope to improve the current ethane cracking technology.

Currently applied reaction temperatures are lower than the found (free) maximum yield temperatures. Therefore the yield is expected to increase with higher temperatures. So, when considering a temperature profile, it might be expected a priori that the isothermal temperature profile pushed to the upper bound is the best candidate. However, the optimisations show that a linear-concave profile is the optimal temperature profile (see figure 7 in

[van Goethem et al. 2010]). The linear-concave profile can be explained by analysing the reaction mechanism. In Figure 1B & D we plotted the ethylene and ethyl (C_2H_5) radical concentrations (the most stable radical for ethane cracking) for respectively the OptPath and IsoT PFR types. The ethyl radical is formed by propagation reactions, H-abstraction reaction of ethane. At higher temperatures ethyl can decompose to ethylene and at lower temperatures it 'reacts' to ethane through an H-abstraction reaction. Other typical reactions of ethyl radicals are the addition to unsaturated bonds and radical termination reactions. Figure 1B and D show that the optimal (OptPath) temperature profile minimises the ethylene and ethyl concentration in the first part of the reaction volumes, which reduces secondary cracking reactions (initialisation reactions and radical addition of C_2H_4) of ethylene. A more detailed discussion on this topic is given in the next section.
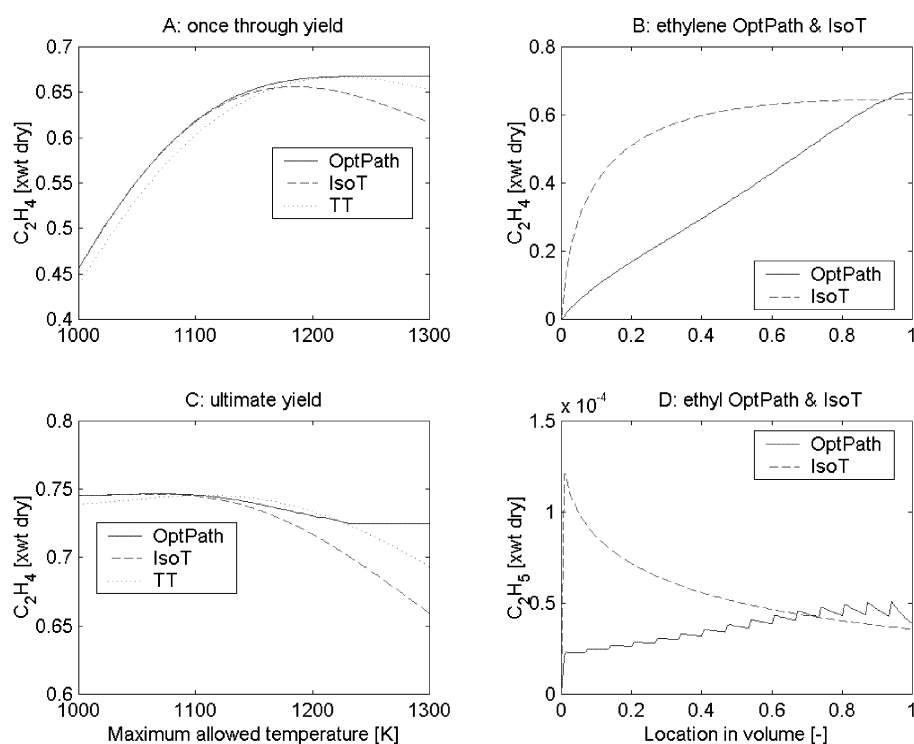

Figure 1: A: Ethylene yield versus maximum allowed temperature (T_{max}). C: Selectivity (or ultimate) ethylene yield as function of T_{max}. B & D: Ethylene and ethylene yield versus scaled reaction volume coordinate at Max T for OptPath & IsoT for the ethane feedstock (adapter from figure 9 in [van Goethem et al. 2010]).

The application of temperatures higher than 1231 K (see Figure 1A) will not generate more ethylene. This implies that the theoretical maximum achievable (once through) ethylene yield for ethane cracking is 66.8%, while the maximum ethylene yield in conventional cracking is typically 55 wt%.

5. KINETIC INTERPRETATION FOR A CONCAVE TEMPERATURE PROFILE

The optimal concave temperature profile discussed and defined in the previous section seems in contradiction with conventional wisdom and it needs a particular attention and kinetic analysis. The isothermal maximum temperature profile is not the optimal one, if the goal is to reach the maximum ethylene yield. Figure 2A and 2B

report predicted ethylene yields and selectivities (moles of ethylene per mole of ethane converted) versus ethane conversion under different isothermal conditions ranging from 1100 to 1400 K.

Two major features can be highlighted in these figures. The first point relates to the ethylene yields (Figure 2A) and it clearly shows that very high temperatures (i.e. 1400 K) are not useful to maximize the ethylene yields. The envelope of these yields indicates an optimal temperature close to 1300 K. The second point, observing the selectivity diagram of Figure 2B, shows that ethylene selectivity decreases when conversion increases, due to the role of secondary reactions.

A kinetic explanation is required to better understand why the initial ethylene selectivity is higher at lower temperatures. Initial ethylene selectivity is higher than 95% at 1100 K and declines to less than 90% at 1400 K. The reason is mainly the rising importance of the initiation reaction of ethane to form methyl radicals:

$$C_2H_6 + [M] \leftrightarrow 2\ CH_3 + [M]$$

Due to the microscopic reversibility, the activation energy of the high pressure limit of this reaction is equivalent to the energy of the primary C-C bond ~89000 kcal/kmol. The role of this reaction increases with rising temperature and it accounts for more than 7% of ethane conversion at 1400 K, while it accounts for only 2% at 1100 K.

For the same reason, Figure 2A also shows that for ethane conversions lower than 90% the optimal temperature is closer to 1200 K, not to 1300 K. Moreover, acetylene and dehydrogenated species, like C_3H_4s (methyl-acetylene and propadiene), butadiene and C_4H_4s are favoured when temperature increases as well. Thus, initial ethylene selectivity would favour lower temperatures but, when conversion rises, it is important to control the successive reactions.
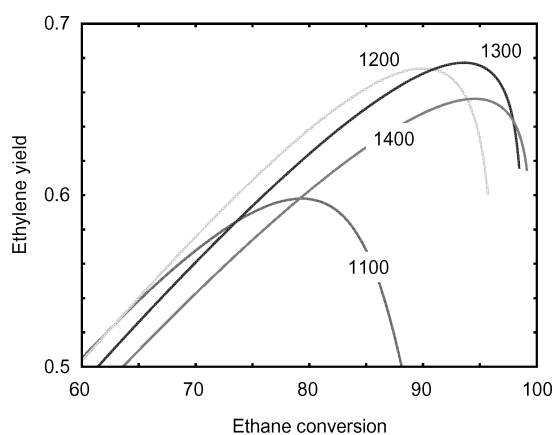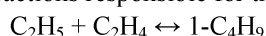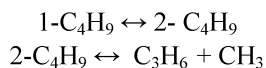

Panel A
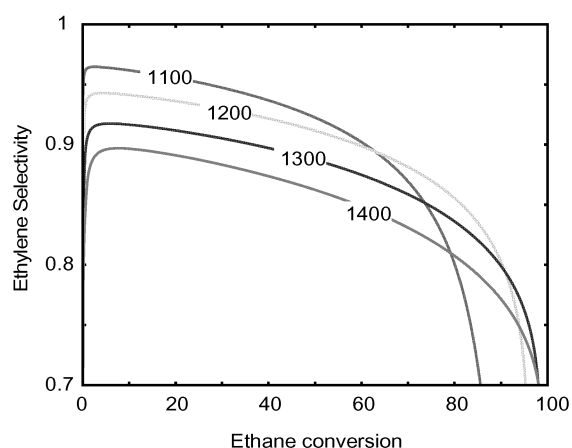
Panel B

Figure 2: Ethane pyrolysis under isothermal temperature profile. Predicted ethylene yields(panel A) and selectivities(panel B) versus ethane conversion at different temperatures [K].

At intermediate conversion, ethyl radical can explain the reduction of ethylene selectivity. Addition reactions of ethyl on ethylene form a 1-butyl radical. Isomerisation reactions between 1- and 2-butyl radicals and successive propylene formation are examples of side reactions responsible for the reduction of ethylene selectivity:

$$C_2H_5 + C_2H_4 \leftrightarrow 1\text{-}C_4H_9$$

$$1\text{-}C_4H_9 \leftrightarrow 2\text{-} C_4H_9$$
$$2\text{-}C_4H_9 \leftrightarrow C_3H_6 + CH_3$$

Dehydrogenation reactions of the two linear butyl radicals to form 1- and 2-butene are of lower relevance. Similarly, for high ethane conversion (i.e. for high ethylene concentrations), the role of the vinyl radical becomes important. In fact, the vinyl addition to ethylene forms the 1-buten-3-yl radical (C_4H_7), responsible together with the methyl-allyl radical of the successive formation of butadiene:

$$C_2H_3 + C_2H_4 \leftrightarrow C_4H_7$$
$$C_4H_7 \leftrightarrow Butadiene + H$$
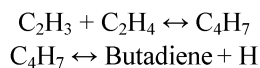
Further addition reactions of the vinyl radical to butadiene, as well as of the C_4H_5 radical to ethylene, explain the formation of cyclopentadiene and benzene:

$$C_2H_3 + Butadiene \leftrightarrow C_6H_9$$
$$C_6H_9 \leftrightarrow Cyclopentadiene + CH_3$$
$$C_6H_9 \leftrightarrow Benzene + H_2 + H$$
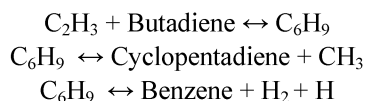
At high severity, that is for high ethane conversion, successive vinyl addition and condensation reactions explain the formation of styrene, naphthalene and poly-cyclic aromatic hydrocarbons (PAH). Figure 3 shows a simplified mechanism of ethane pyrolysis with an indication of the major reaction paths responsible for the possible decrease in ethylene.
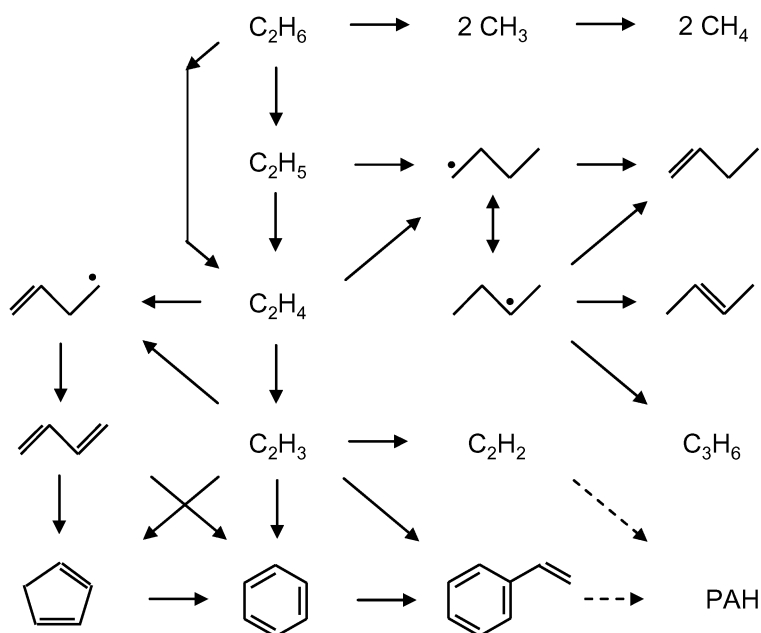

Figure 3: Simplified mechanism of ethane pyrolysis with successive reactions to form heavier species.

In order to better understand the role of the different reactions, *Table 2* reports the yields of the major products when ethylene production is close to its maximum value.

Table 2: Simulation results of ethane pyrolysis in isothermal conditions. Contact time, ethane conversion and yields of major products at maximum ethylene production.

T/K	1100	1200	1300	1400
Time/ms	800	92	12	1.6
Conversion	75.6	87.6	91.2	88.3
Yields (wt%)				
H_2	4.5	5.1	5.2	5
CH_4	6.4	8.6	10.5	10.9
C_2H_2	0.2	1.1	2.4	3.1
C_2H_4	59.2	67.1	67.4	64.2
C_2H_6	24.3	12.4	8.8	11.7
C_3H_4s	0.1	0.1	0.1	0.2
C_3H_6	1.4	1.1	0.9	1.1
C_4H_4	0.1	0.3	0.8	0.8
Butadiene	0.7	1.5	1.8	1.6
Cyclopentadiene	0.4	0.5	0.3	0.2
Benzene	1.1	1.2	1	0.5
Styrene	0.2	0.2	0.1	0.1
Naphthalene	0.4	0.2	0.1	0

A few main elementary reactions to describe the ethane pyrolysis were already discussed since a first pioneering papers on SPYRO kinetic scheme [Dente et al., 1979; Dente et al., 1992] and are summarized in *Table 3*. Note that the kinetic parameters of H abstraction reactions are simply evaluated on the basis of the reactivity of the H abstracting radical and the number and type of H atoms to be abstracted [Ranzi et al., 1994].

Table 3: Main reactions to describe ethane pyrolysis.

	Log A	E [kcal/kmol]
$C_2H_6 + [M] \leftrightarrow 2\ CH_3 + [M]$	17.04	89000
$R + C_2H_6 \leftrightarrow RH + C_2H_5$	$6\ H_{primary}$	
$R + C_2H_4 \leftrightarrow RH + C_2H_3$	$4\ H_{Prim,vinyl}$	
$C_2H_5 \leftrightarrow C_2H_4 + H$	13.9	41000
$C_2H_6 \leftrightarrow C_2H_4 + H_2$	13.9	71000
$C_2H_5 + C_2H_4 \leftrightarrow 1\text{-}C_4H_9$	8.3	7600
$1\text{-}C_4H_9 \leftrightarrow 2\text{-}C_4H_9$	12.5	34500
$1\text{-}C_4H_9 \leftrightarrow 1\text{-}C_4H_8 + H$	13.2	38500
$2\text{-}C_4H_9 \leftrightarrow C_3H_6 + CH_3$	14.0	34000
$C_2H_3 + C_2H_4 \leftrightarrow C_4H_7$	8.55	6000
$C_4H_7 \leftrightarrow Butadiene + H$	13.0	34000
$C_2H_3 + Butadiene \leftrightarrow Cyclopentadiene + CH_3$	8.6	5000
$C_2H_3 + Butadiene \leftrightarrow Benzene + H_2 + H$	8.1	5000

Figure 4 reports the global sensitivity coefficients ($s_{C_2H_4^j}$) of major reactions on the final ethylene yield ($C_2H_4^0$) at 1100 and 1400K. The global sensitivity coefficients is evaluated as:

$$s_{C_2H_4^j} = \frac{C_2H_4^j - C_2H_4^0}{C_2H_4^0} \qquad (4)$$

and it is simply obtained by doubling the kinetic parameters of reaction *j*, according to the brute force method.
The role and effect of the different reactions at the two different temperatures is well highlighted. H abstraction reactions of H radical on ethylene shows a significant negative coefficients, i.e. strongly reduces ethylene yields. The same is true for ethane initiation reaction, mainly at 1400K. H abstractions on ethane, as well as vinyl radical abstractions on H_2 and on C_2H_6, show a positive coefficient and promote ethylene formation. The four centre molecular dehydrogenation reaction of ethane is particularly active at 1400 K.
The maximum reaction temperature in the range of 1200 to 1300K limits the importance of initialisation reactions (i. e. methyl and methane formation) while the linear-concave profile reduces the successive condensation reactions, mainly due to a lower ethyl and vinyl radical concentrations.
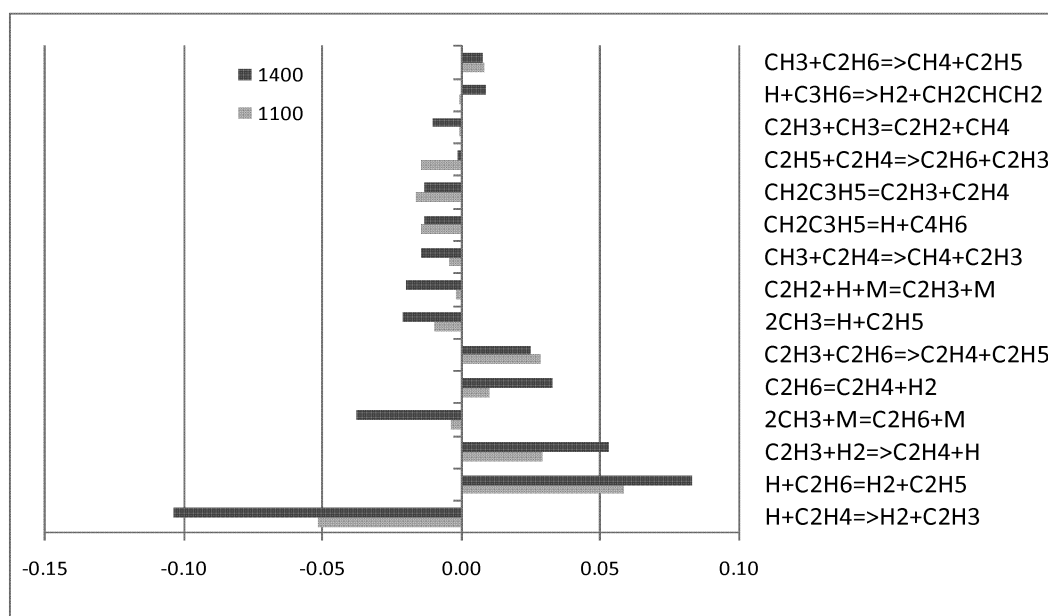

Figure 4: Global sensitivity coefficients on reaction rate coefficients of the final ethylene yield at 1100 and 1400K ("=>" are single direction reactions, "=" are reverse reactions).

6. COMMENTS AND CONCLUSIONS

Although the steam cracking of hydrocarbons is considered to be a mature process, the use of fundamental mechanistic models still gives room to optimise the process conditions in order to increase yields, to reduce by-product formation or to improve run-length conditions. To explore the potential gain in olefin yields under a

higher temperature regime model-based optimization studies were conducted, using a flexible reactor synthesis model (*d*-RMix) and a fundamental kinetic scheme (SPYRO). Rather than finding the expected isothermal temperature profile along the reactor coordinate, it appears that a linear-concave profile with a maximum temperature between 1200 and 1300K is optimal for getting a highest ethylene yield in the steam cracking of ethane. The maximum once through yield that can be achieved is about 67wt%. A separate systematic kinetic analysis reveals that the shape of the temperature profile minimises the successive reactions of the product ethylene to larger side-products, mainly due to a lower concentration of the ethyl and vinyl radicals. The maximum temperature in the range of 1200-1300K is a consequence of limiting the importance of the initialisation reactions.

At temperatures of about 1400K the four centre molecular dehydrogenation reaction and the H-abstraction of ethylene become more important. The confirmative result of this kinetic analysis give further credence to the large scale optimization results for higher olefin yields.

7. NOMENCLATURE

A	Pre-exponential factor [-]
E	Activation energy [cal·mol^{-1}]
F	molar flow rate [mol·s^{-1}]
$F0$	molar flow rate of the feed [mol·s^{-1}]
HC	hydrocarbons
K	product removal function [m^{-3}]
L	feed distribution function [m^{-3}]
$M(V,v)$	mixing kernel (amount mixed from location V to v) [m^{-6}]
Mw	molecular mass [kg·mol^{-1}]
P	pressure [Pa]
R	molar production rate as the net effect of all reactions [mol·m^{-3}·s^{-1}]
s	global sensitivity coefficient [-]
SDR	steam dilution ratio [kg·kg^{-1}]
V	space-time coordinate [m^{3}]
V_t	total volume [m^{3}]
xwt	wet feed mass fractions [-]
xwt_{HC}	hydrocarbon feed mass fractions [-]

7.1 Subscript

j	identifier for the jth feed type [HC, H_2O]
k	identifier for the kth component
V	volume coordinate

7.2 Greek symbols

ϕ_m	total mass flow rate [kg·s^{-1}]

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