

# Reaction path analysis as a tool for scaling up steam cracking coils

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## Abstract

The petrochemical industry is still looking for new methods that predict a detailed product distribution in a number of seconds or minutes for the steam cracking process, especially for heavier feedstocks. Therefore a new direct experimental scale-up method is developed based on the “severity” concept. This method uses two severity indices instead of one to unambiguously characterize the product yields. Indeed at least two indices are needed because two independent variables, the temperature profile and the partial pressure profiles of the reactants in the reactor, determine the reaction rates and hence characterize the product yields. Reaction path analysis indicates that the ethylene to ethane yield ratio is a good measure for the reactants partial pressure, while the  $C_3^-/C_3^+$  ratio is a good measure for the temperature in the reactor. Simulation results for n-butane cracking with a pilot plant reactor, a Lummus SRT-1 reactor and a Kellogg Millisecond reactor show that there is a good agreement for all the product yields if the values of the indices are the same for the different geometries. Further prove is given by the experimental results obtained from a pilot plant reactor and a small scale Uno-Quattro coil.

**Keywords:** Steam cracking, kinetic modeling, scale-up, reaction path analysis

## 1. Introduction

Steam cracking of hydrocarbons is one of the main processes in the petrochemical industry. In tubular reactors hydrocarbons are cracked into commercially more interesting products such as ethylene and propylene. Feedstocks range from ethane to complex mixtures such as naphthas, gas oils and even vacuum gas oils (VGO).

Scaling up steam cracking coils is a difficult task. Two possible methods are commonly applied; mathematical modeling and direct experimental scale-up (Zlokarnik, 2002). Mathematical modeling is probably the most attractive solution because it has the advantage that once the model is developed, results can be easily gathered and computer simulations take only a limited time. One of the major challenges in this method consists of developing a fundamental reaction network. On the one

hand the size of the reaction network can become huge because the number of reactions and species increases exponentially with the average carbon number of the feedstock (Broadbelt et al., 1994). On the other hand, developing these reaction networks implies that both the thermo-chemistry and kinetic parameters have to be known. Moreover fundamental kinetic models work with a detailed feedstock composition and obtaining this information for naphtha's, gas oils and VGO's is not straight forward. These reasons make that direct experimental scale-up is still an interesting option. A commonly applied direct scale-up method is based on the "severity" concept. Scale-up is then performed based on experimental data obtained at the same severity (Shu and Ross, 1982; Szepesy, 1980). However, a single severity index does not unambiguously characterize the yield of the products (Van Damme et al. 1981). In the present contribution reaction path analysis is applied to find a set of independent severity indices which are able to uniquely determine the product spectrum.

## 2. Results and Discussion

### 2.1 Selection of a set of independent severity indices

Product yields depend on process conditions such as feedstock composition, temperature, dilution, total pressure and residence time. The temperature profile and the partial pressure profiles of the reactants in the reactor are the independent variables which determine the reaction rates and hence characterize the product yields. Other process conditions such as residence time or dilution influence the product yields via the temperature profile and/or the partial pressure. The pressure and the dilution influence the partial pressures in an obvious way. Van Damme et al. (1984) and Plehiers and Froment (1987) showed a strong correlation between the residence time and the established temperature profile. The reasoning of the authors can be summarized as follows; cracking at lower residence times is incontrovertibly coupled to higher temperatures for achieving a specific conversion, but it also means that reactions with a high activation energy will be favored, i.e. C-C and C-H  $\beta$ -scission reactions, giving a higher selectivity to light olefins. The selectivity of the heavier products will be lower because they are formed by addition reactions with a relative low activation energy. Thus, the temperature profile influences the residence time in the coil but the residence time is not an independent variable. Also the definition of the residence time  $\theta$  in equation (1) suggests that the residence time is not an independent parameter but a function of the temperature and the pressure profile in the reactor.

$$\theta = \int d\theta = \int \frac{1}{Q} dV = \int \frac{P_t}{F_t RT} dV \quad (1)$$

$\theta$  : Residence time (s)

$V$  : Volume ( $m^3$ )

$Q$  : Volumetric flow rate ( $m^3 s^{-1}$ )

$P_t$  : Total Pressure (MPa)

$F_t$  : Total Molar Flow rate ( $mol s^{-1}$ )

$R$  : Universal gas constant ( $J mol^{-1} K^{-1}$ )

$T$  : Temperature (K)

From the above reasoning, it follows that 2 carefully chosen severity indices might characterize the product yields if one is a measure for the temperature and the other is a measure for the reactants partial pressure in the reactor. A detailed analysis of all the traditional severity indices has shown that the  $C_3^-/C_3^=$  yield ratio can be considered as the best measure of the severity of operation (Van Camp et al., 1985). The  $C_3^-$  fraction contains propylene, propane, propadienes,  $C_2$  components, methane and hydrogen.  $C_3^=$  is the yield of propylene. Van Camp et al. (1985) showed that severity indices such as

the methane yield, the propylene over ethylene ratio or the  $C_3^-/C_3^-$  ratio are all good measures for the conversion and that these severity indices correlate well with the average temperature in the reactor. On the other hand the influence of the reactants partial pressure is not strongly pronounced for these ratios. Hence, the ideal choice for the second index would be a yield ratio which is only dependent on the reactants partial pressure. To identify this severity index reaction path analysis has been applied.

Steam cracking of hydrocarbons is known to proceed through a free-radical mechanism and three important families of reactions can be distinguished:

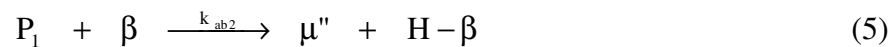
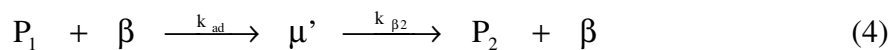
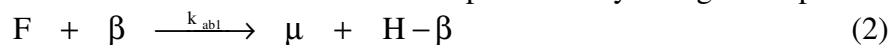
- Carbon-carbon and carbon-hydrogen bond scissions and the reverse radical-radical recombinations
- Hydrogen abstraction reactions, both intra- and intermolecular. Isomerization reactions are considered as intramolecular hydrogen abstractions.
- Radical addition to olefins and the reverse  $\beta$ -scission of radicals, both intra- and intermolecular. Cyclization reactions are considered as intramolecular additions.

In Table 1 characteristic values for the activation energies are given for the different types of reactions. Decomposition reactions are monomolecular reactions with high activation energies. Hydrogen abstraction reactions and addition reactions are bimolecular reactions with low activation energies. Hence, high temperatures and low pressures favor the decomposition reactions, while low temperatures and high pressures favor addition reactions and hydrogen abstractions.

**Table 1:** Characteristic values for the activation energy of the different types of reactions

Reaction Type	Activation Energy (kJ mol <sup>-1</sup> )
Hydrogen abstraction	50
B-scission (C-C bond breaks)	120
B-scission (C-H bond breaks)	170
Addition	20
Isomerization	50

A fundamental description of the steam cracking process is only possible by a complex reaction network involving hundreds of species and thousands of reactions. Reasoning on such a complex mechanism is not possible, therefore a simplified network is proposed. Consider the following simplified reaction scheme where the feedstock is represented by a single component F.



$k_{ab1}$  and  $k_{ab2}$  are the reaction rate coefficients of the hydrogen abstractions,  $k_{ad}$  the reaction rate coefficient of the addition reactions and  $k_{\beta1}$ ,  $k_{\beta2}$  and  $k_{\beta3}$  the reaction rate coefficients for the  $\beta$ -scission reactions.  $\mu$ ,  $\mu'$ ,  $\mu''$  are radicals with a  $\mu$ -character, reacting only via monomolecular reactions,  $\beta$  are radicals with a  $\beta$ -character, reacting only via bimolecular reactions.  $P_1$  are products from the decomposition of  $\mu$ -radicals originating from the feed.  $P_2$  are products formed from addition reactions of  $\beta$ -radicals and products  $P_1$ .  $\beta$ -H are products formed through hydrogen abstraction reactions of  $\beta$ -radicals.  $P_3$  are products formed from hydrogen abstraction reactions from products  $P_1$ .

This simple reaction scheme considers all important reaction possibilities. Cyclization reactions can be considered as internal addition reactions and isomerization reactions as internal hydrogen

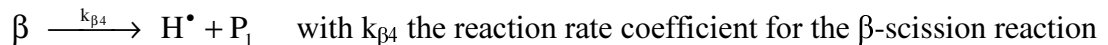
abstractions. No bond scission reactions and recombination reactions have been considered because they do not have an important influence on the product distribution, the hydrogen abstraction reactions, addition reactions, isomerization reactions,  $\beta$ -scission reactions and their relative importance determine the selectivity for the different products.

The products considered in the scheme can be classified in four groups according to the proposed reaction scheme. In Table 2 a classification is shown for the main steam cracking products formed from the cracking of a light naphtha.

**Table 2:** Classification of the main products into 4 groups according to the simplified reaction scheme. [ $P_1$  are products from the decomposition of  $\mu$ -radicals originating from the feed.  $P_2$  are products formed from addition reactions of  $\beta$ -radicals and products  $P_1$ .  $P_3$  are products formed from hydrogen abstraction reactions from products  $P_1$ .  $H-\beta$  are products formed through hydrogen abstraction reactions of  $\beta$ -radicals.]

$P_1$	$P_2$	$P_3$	$H-\beta$
C <sub>2</sub> H <sub>4</sub> C <sub>3</sub> H <sub>6</sub> 1-C <sub>4</sub> H <sub>8</sub> 2-C <sub>4</sub> H <sub>8</sub> i-C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>6</sub> C <sub>6</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>4</sub> C <sub>4</sub> H <sub>6</sub>	H <sub>2</sub> CH <sub>4</sub> C <sub>2</sub> H <sub>6</sub> C <sub>3</sub> H <sub>8</sub> n-C <sub>4</sub> H <sub>10</sub>

In the scheme a distinction is made between two different types of radicals:  $\beta$ -radicals with a  $\beta$ -character and  $\mu$ -radicals with a  $\mu$ -character (Ranzi et al., 1983).  $\mu$ -radicals are radicals which are only reacting in unimolecular  $\beta$ -scission reactions. Large radicals directly formed from the feed have mainly a  $\mu$ -character. This does not mean that reactions such as hydrogen abstractions or addition reactions are not possible, but their reaction rate is a lot smaller than the reaction rate for  $\beta$ -scission. Isomerization reactions are also possible for  $\mu$ -radicals, but after isomerization again a  $\beta$ -scission takes place.  $R_\beta$  radicals are mainly short radicals with 5 or less carbon atoms, which prefer bimolecular reactions such as hydrogen abstractions and addition reactions. These radicals are species such as the hydrogen ( $H^\bullet$ ) and the methyl radical ( $CH_3^\bullet$ ), which do not have any other reaction possibility, or also ethyl ( $C_2H_5^\bullet$ ), propyl ( $C_3H_7^\bullet$ ), vinylic ( $C_2H_3^\bullet$  and  $\nu C_3H_5^\bullet$ ) and allylic ( $C_3H_5^\bullet$  and  $C_4H_7^\bullet$ ) radicals. All the above mentioned small radicals except hydrogen and the methyl radical have also a  $\mu$ -character. The latter is less pronounced and becomes only important at higher temperatures. The reason is that radicals such as the ethyl radical, the secondary propyl radical and the 1-butenyl radical have no C-C bond in  $\beta$  position, but only a C-H bond. Scission of this C-H bond has very high activation energy, i.e. 170 kJ mol<sup>-1</sup>, and hence becomes only important at high temperatures. Consequently these radicals have a  $\beta$ -character at low temperatures, while at high temperatures they have both a  $\beta$ -character and a  $\mu$ -character. At high temperatures the following reaction can be added to the scheme:



Mathematical expressions can be found for the products formed in the simplified reaction scheme if a reactor model is chosen. For simplicity a 1-dimensional reactor model has been used. The yields for the different products  $P_1$ ,  $P_2$ ,  $P_3$  and  $H-\beta$  are given by equations (7), (8), (9) and (10) if the simplified reaction scheme is used.

$$P_1 = \int_0^{\ell} (k_{\beta 1} p_\mu + k_{\beta 4} p_\beta - k_{ad} p_\beta p_{P_1}) dx \quad (7)$$

$$P_2 = \int_0^{\ell} k_{\beta 2} p_{\mu'} dx \quad (8)$$

$$P_3 = \int_0^{\ell} k_{\beta 3} p_{\mu''} dx \quad (9)$$

$$H - \beta = \int_0^{\ell} k_{ab1} p_F p_{\beta} dx \quad (10)$$

$p_F$  is the partial pressure of the feed molecule F,  $p_1$  is the partial pressure of the primary products  $P_1$ ,  $p_{\mu}$  is the partial pressure of  $\mu$  radicals,  $p_{\mu'}$  is the partial pressure of  $\mu'$  radicals and  $p_{\beta}$  is the partial pressure of  $\beta$  radicals.

Taking into account the Pseudo Steady State for the  $\mu'$  radical, see Equation (11), makes that Equation (8) can be transformed into equation (12).

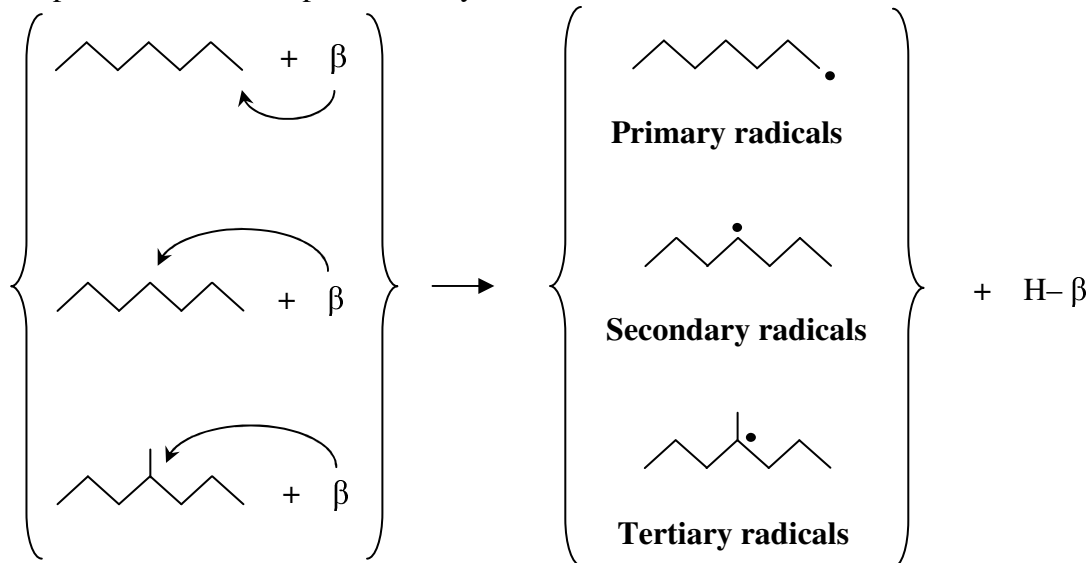
$$\frac{dp_{\mu'}}{dt} = k_{ad} p_{\beta} p_{P1} - k_{\beta 2} p_{\mu'} \approx 0 \quad (11)$$

$$P_2 = \int_0^{\ell} k_{ad} p_{\beta} p_{P1} dx \quad (12)$$

The same can be done for the products  $P_3$ , transforming Equation (9) into Equation (13):

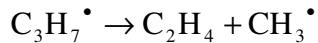
$$P_3 = \int_0^{\ell} k_{ab2} p_{\beta} p_{P1} dx \quad (13)$$

The classification of the products in 4 groups is only a first distinction; in several groups a second distinction is possible. Consider for example the group of products  $P_1$ . A further differentiation is possible based on the type of the  $\mu$ -radical from which the product  $P_1$  originates, i.e. primary, secondary or tertiary. Primary  $\mu$ -radicals give mostly ethylene as primary product, while secondary and tertiary radicals lead to longer olefins. The activation energy for the formation of tertiary and secondary radicals by hydrogen abstractions of the feed is significantly lower than for primary radicals. This will result in different profiles for different  $P_1$  products although they are classified in the same group. This is for example the case for the products ethylene and 1-butene.



**Figure 1:** Different types of radicals as a result of hydrogen abstraction reactions.

In the category of products formed by hydrogen abstraction reactions H- $\beta$  a further differentiation is a direct consequence of the fact that radicals with 2 or more carbon atoms have both a  $\beta$ -character and a  $\mu$ -character at high temperatures. Methane and hydrogen are products originating from pure  $R_\beta$  radicals; hence their yield depends strong on the pressure and increases with increasing temperature. For products such as ethane this is no longer true. At high temperatures, and thus high severities, the ethyl radical can also decompose giving ethylene. The competition of the unimolecular  $\beta$ -scission reactions with the bimolecular hydrogen abstraction for the ethyl radical make that both the temperature and the pressure have a strong influence on the ethane yield. The same reasoning also holds for products such as propane. Propane is formed via hydrogen abstraction reactions of propyl radicals, but here an extra  $\beta$ -scission is possible of the propyl radical:



This reaction has a significantly lower activation energy (120 kJ mol<sup>-1</sup>) then the activation energy of  $\beta$ -scission reaction of the ethyl radical (170 kJ mol<sup>-1</sup>). Hence, the yield for propane is a factor 5 smaller then the yield for ethane.

The fact that the ethyl radical cannot decompose via a C-C  $\beta$ -scission makes it an interesting radical. This special behavior can be used with great advantage. The ratio of the ethylene yield to the ethane yield is then an indication which path is preferred for the ethyl radical; at low partial pressures and high temperatures this is the ethylene route, at high partial pressures and low temperatures it is the ethane route. This can also be concluded from the mathematical expressions deduced from the simplified reaction scheme. The following mathematical expression can be found for the ethylene to ethane ratio ( $C_2H_4/C_2H_6$  ratio) using the symbols from the simplified reaction scheme if a one-dimensional reactor model is assumed:

$$\frac{C_2H_4}{C_2H_6} = \frac{\int_0^1 (k_{de1,\mu} p_\mu + k_{de3,\beta} p_\beta - k_{ad} p_\beta p_{P_1}) dx}{\int_0^1 (k_{abl} p_F p_\beta) dx} \quad (14)$$

Ethylene is formed via monomolecular  $\beta$ -scission reactions and disappears via bimolecular addition reactions. Ethane is formed via bimolecular hydrogen abstractions. Hence, it is obvious that modifying the partial pressure of the reactants has a strong influence on the ethylene to ethane ratio. For instance, if the dilution is increased, the monomolecular reactions leading to ethylene formation are favored to the bimolecular reactions giving ethane and consuming ethylene. Consequently the value of the ethylene to ethane ratio considerably increases. This fact suggests that the ethylene to ethane ratio is a possible severity index which is strongly influenced by the partial pressure of the reactants. It would be ideal if the temperature dependence of this ratio would be neglectable. This is not true, higher temperatures favor decomposition reactions over addition and hydrogen abstraction reactions, making the ratio rise. On the other hand because the dependence of the  $C_3^-/C_3^-$  ratio on the partial pressure of the reactants is weak a combination of the ethylene to ethane yield ratio with the  $C_3^-/C_3^-$  ratio could characterize the product yields in a unique way. Validation of this approach for changing the scale has been carried out using both experimental and simulation results for a wide range of reactor geometries. Simulations with a 2-dimensional reactor model were performed for n-butane cracking in different reactor geometries, aiming at the same values for the same ethylene to ethane yield ratio and the same  $C_3^-/C_3^-$  ratio. The experimental data for a light naphtha feedstock are used to illustrate that 1 severity index is not enough, but that a combination of the ethylene to ethane yield ratio and the  $C_3^-/C_3^-$  ratio unambiguously characterize the product yields.

## 2.2 Validation

Simulations were performed with a 2-dimensional reactor model to test the new approach as a method for scaling-up steam cracking coils. The use of a 2-dimensional reactor model is necessary because important radial gradients exist in industrial tubular reactors, not only for the temperature but also for the molecular and in particular for the radical species making the 1-dimensional reactor model insufficient (Van Geem et al., 2004). The reactor model equations and the details about the calculation of the velocity profile, the conductivity, the diffusivity,... are specified in Van Geem et al. (2004).

**Table 3:** The characteristics for the different reactors, the conditions used for realizing the same value of both the  $C_3^-/C_3^-$  ratio and the  $C_2H_4/C_2H_6$  ratio, and the simulated product yields and conversion for the cracking of pure n-butane

	<b>Lummus SRT-I reactor</b>	<b>Pilot Reactor</b>	<b>4-2-1 Split coil</b>
<b>Reactor length (m)</b>	100.96	12.38	40
<b>Tube diameter (cm)</b>	12.4	0.9	7.6 – 11.4 – 15.2
<b>Wall thickness (mm)</b>	0.008	0.002	0.005
<b>CIP (MPa)</b>	0.3	0.3	0.3
<b>CIT (K)</b>	873	873	873
<b>COT (K)</b>	1130	1139	1139
<b><math>\delta</math> (kg steam/kg HC)</b>	0.77	0.85	0.71
<b>Flow rate (kg/h)</b>	3500	4	5000
<b>Residence time (s)</b>	0.575	0.363	0.273
<b>RATIO'S (wt % / wt %)</b>			
<b><math>C_3^-/C_3^-</math> ratio</b>	4,54	4,54	4,54
<b><math>C_2H_4/C_2H_6</math> ratio</b>	9,20	9,20	9,21
<b>CONVERSION</b>			
<b><math>C_4H_{10}</math> conversion</b>	92.4	92.6	92.5
<b>PRODUCT YIELDS (wt %)</b>			
<b>CH<sub>4</sub></b>	20,8	21,0	20,9
<b>C<sub>2</sub>H<sub>4</sub></b>	34,5	34,8	34,7
<b>C<sub>2</sub>H<sub>6</sub></b>	3,7	3,8	3,8
<b>C<sub>3</sub>H<sub>6</sub></b>	17,6	17,8	17,7
<b>C<sub>4</sub>H<sub>6</sub></b>	2,7	2,6	2,8
<b>1-C<sub>4</sub>H<sub>8</sub></b>	1,5	1,5	1,5
<b>C<sub>6</sub>H<sub>6</sub></b>	2,7	2,5	2,6

The simulations were performed for different reactor geometries, aiming for the same value of the  $C_3^-/C_3^-$  ratio and the same value of the ethylene to ethane yield ratio in the different configurations. The considered reactors were the following: a pilot plant reactor, a Lummus SRT-I reactor and a 4-2-1 split coil. The characteristics for the reactors used in the simulations and the conditions used for realizing the same value of both the  $C_3^-/C_3^-$  ratio and the ethylene to ethane yield ratio ( $C_2H_4/C_2H_6$ ) are specified in Table 3. As feedstock n-butane was chosen for a number of reasons:

1. The composition of a naphtha feedstock can vary over a broad range. Also the number of components in a naphtha feedstock is huge, making the reaction network enormous. For n-butane the reaction network is still manageable, containing only a hundred species and thousand reactions
2. The product spectrum obtained with n-butane is very similar in respect to the one obtained for a naphtha feedstock.
3. Looking at a single compound is a more severe test case because no compensation effects can take place. With the latter is meant that for example the lack of conversion of one feed molecule is compensated by a higher conversion of another.

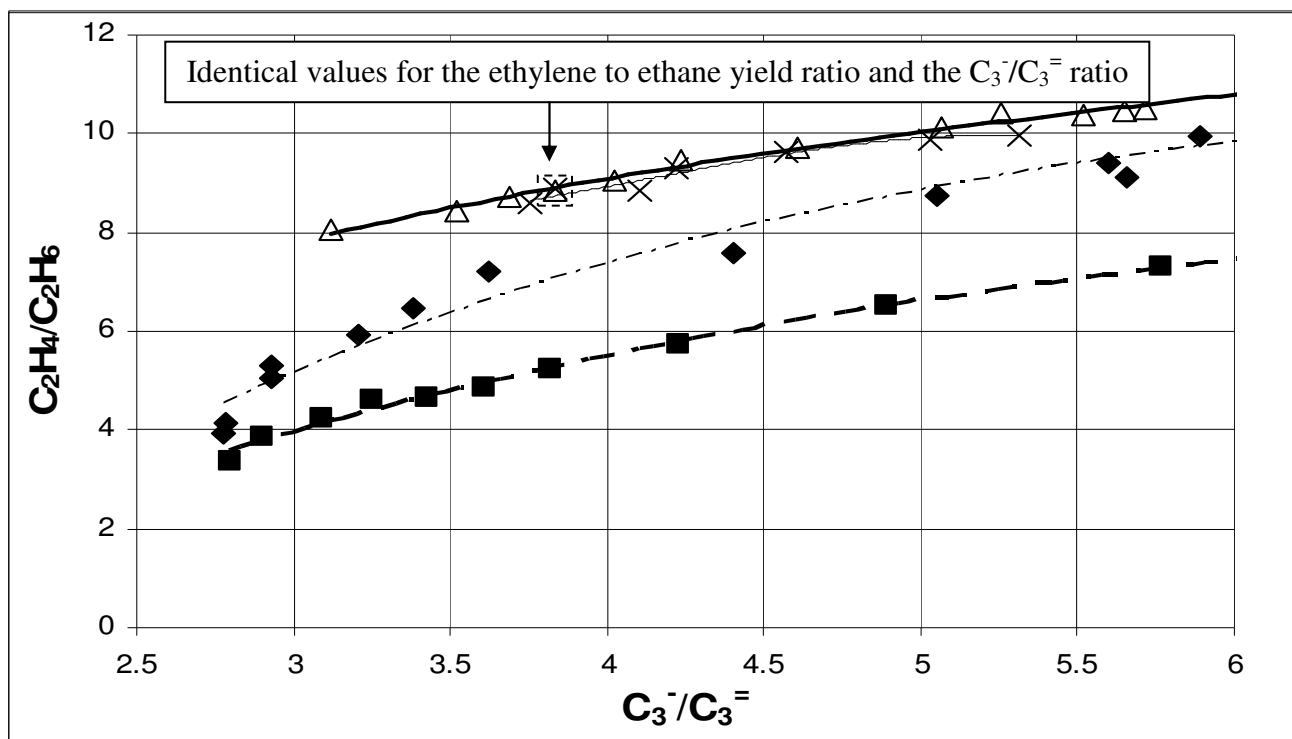
The results in Table 3 for the product yields and the conversion show that there is a good agreement for all of the different reactors. It has to be stressed that this result is remarkable because of the huge difference in size of the selected reactors. Not only the reactor length but also the diameter and even the configuration differ significantly for the three reactors. For example the length of the reaction section of the largest coil, the Lummus SRT-I (100,96 m long), is more than eight times larger in respect to the length of the smallest one, the LPT pilot plant (12,38 m). Also the residence time in the different reactors varies strongly; from 0.577 s in the Lummus SRT-I reactor, over 0.363 s in the pilot reactor and 0,273 s in the 4-2-1 split coil. Hence, it is obvious that direct experimental scale-up for the steam cracking process does not require identical values for the residence time.

The same good agreement is also observed experimentally. Two different reactor geometries have been used to crack the same naphtha feedstock; a traditional single coil reactor of 23 m long and the compact, 4 m long Uno-Quattro coil (Plehiens and Froment, 1991). The conditions in the traditional single coil reactor have been varied to realize the same  $C_2H_4/C_2H_6$  ratio and the same  $C_3^-/C_3^=$  ratio as in the Uno Quattro coil. In Figure 2 the  $C_2H_4/C_2H_6$  ratio is plotted versus the  $C_3^-/C_3^=$  ratio for both reactors. These results clearly show that using a single severity index is not enough. For a single value of the  $C_3^-/C_3^=$  ratio different values for the ethylene to ethane yield ratio are possible and vice versa. For a flow rate of  $2.1 \text{ kg h}^{-1}$  and a dilution of  $0.8 \text{ kg / kg}$  in the traditional single coil reactor the variation of the ethylene to ethane yield ratio versus the  $C_3^-/C_3^=$  ratio is almost identical of the profile obtained with the Uno-Quattro coil. In a specific case, see Figure 2, the same value for the ethylene to ethane yield ratio and the same value for the  $C_3^-/C_3^=$  ratio are experimentally observed for the different reactors. The product yields corresponding to these experiments are specified in Table4. A good agreement is noticed between the product yields obtained in the pilot plant and in the Uno-Quattro coil despite the differences in the operating conditions and the geometry of the reactors.

**Table 5:** Product yields for the in the LPT pilot plant and the Uno-Quattro coil.

	Single Coil Reactor	Uno-Quattro coil
$C_3^-/C_3^=$ ratio	3.83	3.84
$C_2H_4/C_2H_6$ ratio	8.81	8.85
PRODUCT YIELDS (wt %)		
CH <sub>4</sub>	13.36	13.04
C <sub>2</sub> H <sub>4</sub>	3.20	3.23
C <sub>2</sub> H <sub>6</sub>	28.24	28.57
C <sub>3</sub> H <sub>6</sub>	16.69	16.74
C <sub>4</sub> H <sub>6</sub>	4.69	4.83





**Figure 2:** The course of the ethylene to ethane yield ratio ( $C_2H_4/C_2H_6$ ) as function of the  $C_3^-/C_3^-$  ratio. Results corresponding to naphtha cracking experiments carried out in a single coil reactor and the Uno-Quattro coil. [■ Single coil reactor. Flow rate:  $4.3 \text{ kg h}^{-1}$ , dilution:  $0.2 \text{ kg steam/ kg HC}$ ; ◆ Single coil reactor. Flow rate:  $3.2 \text{ kg h}^{-1}$ , dilution:  $0.4 \text{ kg steam/ kg HC}$ ; △ Single coil reactor. Flow rate:  $2.1 \text{ kg h}^{-1}$ , dilution:  $0.8 \text{ kg steam/ kg HC}$ ; × Uno-Quattro coil. Flow rate:  $5.5 \text{ kg h}^{-1}$ , dilution:  $0.6 \text{ kg steam/ kg HC}$ ]

It can be concluded from the preceding simulations and experiments that the  $C_3^-/C_3^-$  ratio and the ethylene over ethane yield ratio are independent indices and that they unambiguously characterize the observed product yields. Using a third parameter is not necessary.

### 3. Conclusion

A new method for transferring experimental data from one unit to another is developed for the steam cracking process. This direct scale-up method is based on the “severity” concept. Scale-up is then performed based on experimental data obtained at the same severity. However, a single severity index does not unambiguously characterize the product yields. Therefore reaction path analysis is applied to find a set of independent severity indices which are able to uniquely determine the product spectrum. The temperature profile and the partial pressure profiles of the reactants in the reactor are the independent variables which determine the reaction rates and hence characterize the product yields. This suggests that working with 2 carefully chosen severity indices is sufficient to unambiguously characterize the product yields if one severity index is a measure for the temperature and another index is a measure for the reactants partial pressure. A detailed analysis of all the traditional severity indices has shown that the  $C_3^-/C_3^-$  yield ratio can be considered as one of the best measures for the conversion and hence for the temperature in the reactor. On the other hand the dependence of this ratio on the reactants partial pressure is weak, making the  $C_3^-/C_3^-$  ratio a good choice as first severity index. As a second severity index the ethylene to ethane yield ratio is chosen. Reasoning on a simplified model shows that this ratio is a good measure for the reactants partial pressure. Hence, a combination of the  $C_3^-/C_3^-$  ratio and the ethylene over ethane yield ratio have the potential to characterize the product

yields in a unique way. The results obtained in one reactor can thus directly be used without any mathematical treatment if both the  $C_3^-/C_3^-$  ratio and the ethylene to ethane yield ratio have the same value. This is proven by the simulation results for n-butane cracking with a pilot plant reactor, a Lummus SRT-1 reactor and a Kellogg Millisecond reactor. Experiments with a pilot plant reactor and the compact Uno-Quattro coil further show that one severity index is not enough, but that the values of the  $C_3^-/C_3^-$  ratio and the ethylene over ethane yield ratio for a specific feedstock unambiguously characterize the observed product yields. This has huge implications for scaling up steam cracking coils. It implies that if the  $C_3^-/C_3^-$  ratio and the ethylene over ethane yield ratio have the same value for 2 different reactors all the product yields are equal.

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