Towards Synthesis of an Optimal Thermal Cracking Reactor
Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Towards Synthesis of an Optimal Thermal Cracking Reactor

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Abstract

To develop new reactor options for thermal cracking of ethane or other light hydrocarbons to lower olefins a fundamental process synthesis approach is taken. Firstly, an optimal reaction path and conditions are targeted, starting from a mechanistic reaction network. Secondly, to implement the optimal reaction path the reactor geometry and equipment are designed. This contribution focuses on the development of a targeting approach, for which a new distributive reaction-mixing synthesis model is formulated and applied. The mixing kernel in the model provides freedom to redistribute the reaction mixture along a continuous reaction coordinate to optimize product yield. The model reproduces the results for the Van de Vusse reaction network as obtained by the attainable region theory. When applied to a small reaction network for the conversion of ethane into ethene, it reconfirms the existing result that for this network the plug flow mode at maximum temperature and minimum pressure gives the optimal olefin yield.

Keywords: reactor synthesis, targeting, distributive reaction-mixing, attainable region, thermal cracking.

Introduction

This paper outlines an approach to the synthesis of an optimal reactor for thermal cracking of ethane and other light hydrocarbons to lower olefins. The synthesis objective is, given the mechanistic process reaction network and the feed sources, to maximise the amount of product per unit mass of feed.
We apply a fundamental approach which can be divided into two steps. The first step, targeting, is the determination of the optimal reaction path and conditions along a reaction coordinate in composition space, using reaction and mixing operations. The results are the product yield, as obtained from the optimal degree of mixing, the feed distribution function, the temperature profile, pressure profile and the residence time. In the second step we translate this optimal path in the required geometry for (new) equipment. In this paper we will concentrate on the first step. This approach, which

suffices for a system of single thermodynamic phase, is compatible with the more extensive design approach of Krishna and Sie (1994) for multi-phase reaction systems.

There are a couple of reasons for developing and trying a new reactor synthesis model for targeting. Conceptually it seems attractive to find a general representation of the conversion process, which contains the standard ideal reactor types (batch, CSTR, distributive PFR) as limiting parametric cases and which is capable of combining such reactor types seamless in a single conversion "hull". Furthermore, the use of a synthesis model with continuous variables only (avoiding discrete synthesis decision variables) is computationally attractive in simulation and optimization calculations. The essence of the new reactor synthesis model is the parallel consideration of reactions and distributive mixing, feed allocation and product removal along a reaction progress coordinate.

In our synthesis approach the determination of the optimal reaction path is decomposed in three stages:
a. Identification of the feasible window of physico-chemical conditions with a definition of a relevant product yield;
b. Determine the optimal species distribution and product yield by running the reactions along a suitable reaction progress coordinate (e.g, space-time or reaction volume) for pre-specified temperature and pressure profiles and by varying the distributions of the feed injection, of the product removal and internal mixing
c. Determine the optimal temperature, pressure profiles and re-optimise the second stage till consistency is obtained.

Our motivation for the first stage (*a*) is to identify the feasible range of operating conditions with a target, like: what is a practically relevant product yield, under what conditions (*T, P, C*) is the mechanistic reaction scheme applicable, catalyst used, number of phases, what type of heat transfer is allowed, can we allow discontinuities in temperature & pressure profiles, what is the limiting temperature and pressure for the best engineering materials available, etc.. The outcome of stage (*a*) is a set of feasibility constraints with a value function for the next synthesis stages.

Physical considerations imply that the information from the stages (*b,c*) should be computed simultaneously. Since we will be researching a complex system, thermal cracking described by an extensive radical mechanism, containing strongly non-linear interactions between temperature and composition related variables, we propose to separate stages (*b*) and (*c*) in order to obtain partial optimisation problems that can be solved more easily. The optimisation of the *T* and *P* profiles is difficult for large reaction systems. This decomposition in two stages requires verification and re-iteration if the outcome of stage (*c*) influence the results obtained at stage (*b*)

Applying a new method to determine the mixing behaviour and the distribution of the feed we will explain it in the next chapter where we also compare it with other known synthesis methods. Thereafter we apply the synthesis model to the determination of the optimal reaction path for the thermal cracking of ethane. Because we are exploring this methodology we use first a small kinetic model from the literature in order to keep the computational challenges limited. This is a preparatory step towards applying the proposed methodology to a large scale, rigorous kinetic scheme,

SPYRO®, which is used in the industry (Dente and Ranzi (1979), van Goethem et al. (2001))

Distributive reaction-mixing model (*d*-RMix)

In the synthesis of a reactor the optimal species distribution and product yield need to be determined. We propose a distributive, continuous species balance equation (1) that describes convective transport, reactions and the joint distributed injection of the feed, product removal and mixing (Grievink (2003)). These distributions are enabled by the introduction of two functions and one kernel namely: the first function for the feed distribution (*L*), the second function for the product removal (*K*) and a kernel for the mixing (*M*). Therefore we called this equation the distributive reaction-mixing model (*d*-RMix) The derivation of this equation is given in appendix A.

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} + L(V)F0_k - K(V)F_{k,V} +$$

$$\int_0^{V_t} \left(F_{k,v} M(v,V) - F_{k,V} M(V,v) \right) dv \tag{1}$$

In equation (1) the independent coordinates are:
t (s)   is time,
V (m³) is the space-time coordinate here as expressed as an increasing reaction volume, where this reaction volume ranges between zero and an upper bound, the total volume V_t (m³).
The subscript k is the identifier for k^{th} component.

The dependent variables are:
C (mol·m⁻³),   the molar concentration,
F_{net} (mol·s⁻¹)   the net molar flow rate,
R (mol·m⁻³·s⁻¹),   the molar production rate as the net effect of all reactions,
F (mol·s⁻¹)   the total molar flow rate,
L (m³)   the feed distribution function,
$F0$ (mol·s⁻¹)   the molar flow rate of the feed,
$M(V,v)$ (m⁻⁶)   the mixing kernel (amount mixed from location V to v),
K (m³)   product removal function.

The first term of equation (1) describes the molar accumulation of the kth component per unit reaction volume. The second term represents the convective transport (which may also be extended to include gradient driven diffusion terms),
The third term covers the net rate of formation of the kth component due to the joint effect of all reactions (stoichiometric summation over all volumetric reaction rates).
The fourth term indicates the distributive injection of the feed over the total available reaction volume.
The fifth term accounts for a distributive removal of reaction material along the reaction coordinate; e.g. at locations where the product flow has a (local) maximum. It is not a separation function because it does not account for selective removal of species, like by means of membranes.

The sixth and the seventh term model the distributive re-allocation of reaction material from one location (V) to another one (v). This is called "distributive mixing". The sixth term represents the material coming in at the reference location V from all other locations. The seventh term accounts for the local reaction mixture distributed to all other locations (outgoing). The mixing allows for bypassing and back mixing of varying level of intensity.

The supply and removal functions L and K are made spatially dependent. Temporal dependency, relevant in case of dynamic operations like start up en shutdown strategies, is ignored. The mixing kernel M is considered a property of the geometry and therefore cannot be temporal dependent.
Since the supply and removal functions, L, K and the mixing kernel M, represent flows, they are independent of the species. But they are subject to physical feasibility constraints (see, appendix A). To prevent negative flow rates the supply and removal functions, L and K, should have non-negative values. A constraint is added to ensure that the total of the available feed is released in the reaction volume. The mixing kernel, M, should be non-negative and bounds are imposed on the maximum value. A special condition defines the preservation of mass. It is obvious that the forward and backward mixing should neither change the conservation of mass (by artificially creating mass as a mathematical incident) nor give rise to negative flows. These conditions impose upper bounds on the mixing kernel M.

The distributive reaction-mixing model (d-RMix) contains four state vectors, C, F_{net}, F, R, and therefore three additional equations need to be defined:
1. Relations between, net rates of formation R, and concentrations, C, are provided by the stoichiometric scheme and reaction kinetics.
2. Relations between concentrations, C, and molar flow rates, F_{net}, can be established for the gas phase systems at atmospheric pressures by means of the ideal gas law, linking molar density and molar fractions to concentrations
3. Relation of the net, F_{net}, and the total molar flow rates, F, these are provided by the d-RMix and can be found in appendix A, equation (22).

When augmenting the species balances with these equations, and associated boundary and initial values, a complete set of equations is obtained. The degrees of freedom for decision making in synthesis are given by the supply and removal functions and the mixing kernel.

The second stage (b) of the reactor synthesis problem is now made up by the above set of model equations, the feasibility constraints on the process conditions and on the supply and removal functions and the mixing kernel. The stoichiometry and the reactions kinetics are assumed to be known, with given specified temperature and pressure profiles. Using the product yield as a target value function to be optimised the synthesis degrees of freedom, K, L, M, can be determined. Since there infinitely many degrees of freedom the synthesis optimisation problem is reduced to a finite dimensional one by discretisation of reaction volume coordinate.(see Figure 8 in Appendix A).

Distributive reaction-mixing model (*d*-RMix) –Ideal reactors

The generic nature of the distributive reaction-mixing model should allow for a reduction to the ideal reactor types. We show in detail in appendix B how the ideal reactor models, the PFR and the DSR, are straightforwardly derived. The derivation of the CSTR is less straight forward. We have validated this result with the Van de Vusse (1964) reaction scheme as given by (Kauchali et al. (2002)):

$$A \xrightarrow{k_1=1} B \xrightarrow{k_2=1} C$$
$$2A \xrightarrow{k_3=10} D \tag{2}$$

The desired product is *B*, while *C* and *D* are considered by products. The molar production rates are given by

$$R_A = -k_1 C_A - 2k_3 C_A \tag{3}$$

$$R_B = k_1 C_A - k_2 C_B \tag{4}$$

$$R_C = k_2 C_B \tag{5}$$

$$R_D = k_3 C_A \tag{6}$$

We assume steady state and constant density and temperature. The flow rate entering the reactor is $F0 = [1, 0, 0, 0]$ mol·s^{-1}. The relation between molar flow rate and concentration is given by:

$$F_i = C_i \frac{\phi_m}{\rho} \tag{7}$$

Were ϕ_m, ρ are respectively the mass flow rate and the density. We define the volumetric flow rate entering the reactor to be unity. This implies that the value of the concentration is equal to the molar flow rate (at the boundary). The mass flow rate is proportional with: $\phi_m \propto F_A + F_B + F_C + 2F_D$. Therefore the concentrations can be evaluated with the following relation:

$$C_{i,V} = \frac{F_{i,V}}{F_{A,V} + F_{B,V} + F_{C,V} + 2F_{D,V}} \qquad V \in [0, V_t] \tag{8}$$

Figure 1 shows the results of the comparison between the analytical solution and the solution obtained with the distributive reaction-mixing model (*d*-RMix). Each solution point of the *d*-RMix is a solution of (34) with a different total volume. We conclude that the CSTR results are properly predicted.
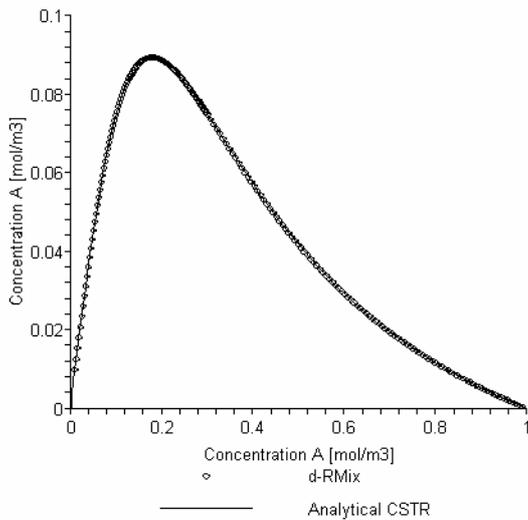
Figure 1 : Concentrations of A and B for the analytical CSTR and *d*-RMix results for van de Vusse scheme (1, 1, 10).

Relation of the distributive reaction-mixing model (*d*-RMix) with the attainable region theory

The attainable region is defined as the full set of product composition vectors that can be achieved by all possible steady state reactor networks, using only the processes of reaction and mixing (Kauchali et al. (2002)). Feinberg and Hildebrandt (1997) have shown in their paper that the conventional reactors, PFR, CSTR and differential side stream reactors DSR, shape the boundaries of the attainable region. The synthesis is determined by optimisation of discrete reactor superstructures, with geometric techniques (Hildebrandt and Glasser (1990), Kauchali et al.(2002)), more recently the method of bounding hyperplanes and IDEAS (Abraham and Feinberg (2004), Zhou and Manousiouthakis (2006)) have been proposed.

In the previous 2 paragraphs we have demonstrated that the *d*-Rmix embodies these three reactor types. To demonstrate the capabilities of our *d*-Rmix we have determined the attainable region for the kinetic scheme (2), which is also reported by Kauchali et al. (2002). Figure 2 shows the both results, each point in the profile for the *d*-RMix is the outcome of an optimisation problem. The objective of this optimisation was to maximise the concentration of *B* at the exit of the reactor by adjusting the mixing kernel *M* and feed distribution function *L*. The effluent removal function, *K*, was defined zero, the total volume was set to an arbitrary value of 0.3 m^3, and the exit concentration of *A* was fixed to the desired value. This is possible by using the volumetric flow rate entering (constant density) the reaction volume as a degree of freedom.

The simulator/optimiser used in this work is described by Van Goethem et al. (2002). We apply an equation based approach, which means that we approximate the solution with the technique orthogonal collocation of finite elements (OCFE), yielding a set of non-linear algebraic equations that can be solved and/or optimised. The mixing

kernel, *M*, is approximated as piecewise linear. The model is coded such that the number of piecewise linear sections can be set independently of the number of finite elements of the OCFE method. This is done in order to be able to increase the modelling detail there were steep gradients occur. At the bounds of the piecewise linear sections of *M* the *L* and *K* can be active to inject or remove fluid.
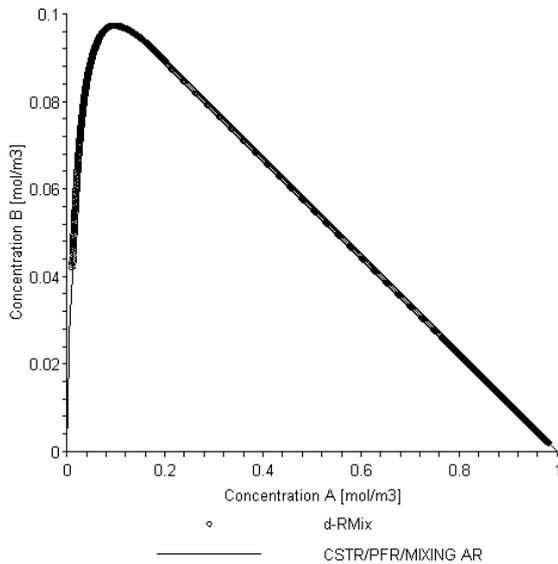
Figure 2: Attainable region for van de Vusse system [1, 1, 10] by CSTR/PFR/MIXING and *d*-RMix.

We again solved the van de Vusse system (2) with a different set of kinetic constants [10, 1, 0.145]. Figure 3 shows the comparison of the results obtained with the geometrical method using CSTR, PFR and mixing as the basic blocks and the *d*-RMix. On the basis of these to cases we conclude that the *d*-RMix can predict attainable regions.
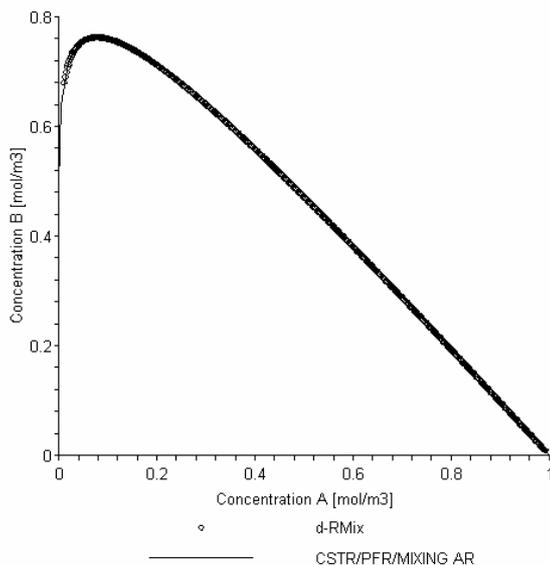
Figure 3: Attainable region for van de Vusse system [10, 1, 0.145] by CSTR/PFR/MIXING and *d*-RMix.

Testing by application to thermal cracking process using a small reaction network

Having introduced and tested the *d*-RMix we will discuss its application to thermal cracking of ethane. This process is also called steam cracking or steam pyrolysis. The process consists of converting hydrocarbons (typically alkanes, cyclo-alkanes, gas oils, vacuum gas oils) in the presence of steam to ethene, propene, hydrogen, methane and a large number of heavier alkenes, alkanes and aromatics. The state-of-the-art process is performed in multiple parallel tubular reactors (also called radiant coils) placed in a furnace (also called firebox or radiant box). The hydrocarbons mixed with steam, flow through the radiant coils with a residence time of 100-1000 milliseconds and a feed rate per coil for the hydrocarbons of approximately 200 - 2.000 kg·h^{-1} at a pressure of ~ 1-4 bars. Within the radiant coil the mixture is heated from ± 850 K to ± 1150 K and therewith cracked (dehydrogenated) to smaller unsaturated hydrocarbons. At the coil exit the reaction mixture is rapidly quenched to preserve the composition. The major product of the process is ethene. The ethene yields range from 20 - 50 wt%. For a more elaborated review of this process the reader is referred to Van Goethem et al. 2007.

As mentioned in the introduction we will initially use a small kinetic scheme found in the literature (Froment and Bischoff (1979)) for testing purpose, this scheme is given in Table 1.

i-th	Reaction	Order	ko_i [s^{-1}] or [m^3·mol^{-1}·s^{-1}]	Ea_i [J·mol^{-1}]
1.	$C_2H_6 \rightarrow C_2H_4 + H_2$	1	$4.65 \cdot 10^{13}$	273,020.0
2.	$C_2H_4 + H_2 \rightarrow C_2H_6$	2	$8.75 \cdot 10^5$	136,870.0
3.	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	1	$3.85 \cdot 10^{11}$	273,190.0
4.	$C_3H_6 \rightarrow C_2H_2 + CH_4$	1	$9.81 \cdot 10^8$	154,580.0
5.	$C_2H_2 + CH_4 \rightarrow C_3H_6$	2	$5.87 \cdot 10^1$	29,480.0
6.	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$	2	$1.03 \cdot 10^9$	172,750.0
7.	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	2	$7.08 \cdot 10^{10}$	253,010.0

Table 1: Reaction scheme and kinetic parameters for thermal cracking of ethane (Froment and Bischoff (1979))

The stoichiometric coefficient matrix of the reaction system is defined by:

$$\alpha = \begin{pmatrix} 0 & 0 & 1 & -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & -2 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & -1 & -1 & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad (9)$$

The individual reaction rates are determined by

$$r_i = k_i \prod_{j=1..n} C_j^{\kappa_j} \qquad \kappa_j = \begin{cases} 1 & \alpha_{i,j} < 0 \\ 0 & else \end{cases} \qquad i = 1..n_{reac} \qquad (10)$$

Were the reaction constants are defined by the Arrhenius equation:

$$k_i = ko_i \exp\left(\frac{-Ea_i}{RT}\right) \qquad i = 1..n_{reac} \tag{11}$$

The molar production rate of the nine components is computed according:

$$R_i = \sum_{i=1}^{n_{reac}} \alpha_{ij} r_i \quad i = 1..n \tag{12}$$

The concentrations can be related to the molar flow rates with the aid of the ideal gas law:

$$C_i = \frac{F_i}{\sum_{j=1..n} F_j} \frac{P}{RT} \qquad i = 1..n \tag{13}$$

The feed flow rate of the feed and the component numbers are defined in Table 2. The feed is considered of pure ethane (*HC*) with a steam to oil (*STOR*) ratio of 0.5.

Component	CH_4 [kg]	C_2H_2 [kg]	C_2H_4 [kg]	C_2H_6 [kg]	C_3H_6 [kg]	C_3H_8 [kg]	C_4H_6 [kg]	H_2 [kg]	H_2O [kg]
Number	1	2	3	4	5	6	7	8	9
$F0$ [mol·s^{-1}]	0	0	0	HC	0	0	0	0	HC·STOR

Table 2: The component numbers and the feed flow rate definitions.

Stage a: Identification of the feasible window of physico-chemical conditions

As mentioned several hydrocarbon feed stocks can be used for thermal cracking. In this research we have limited ourselves to ethane due to the availability of small kinetic schemes in the literature and the explorative nature of the research to the *d*-RMix model. The maximum allowed tube skin temperatures, approximately 1300 – 1350 K, depend on the metallurgic properties of the radiant coils. In the future we expect that new or better materials will be come available and therefore the maximum process fluid temperature is considered to be 1300 K, instead of ~1150 K. When indirect heat is applied, like in current cracking furnaces, the tube skin temperature will than be approximately 1450-1500 K. Vacuum is considered not to be an option because of the large throughput of an ethylene plants therefore the pressures should be larger than 1 bar. The distribution of the feed is considered to be possible at discrete locations. Removal of process fluid is assumed not to be an option. This process is a high temperature process and coking is an important side effect of thermal cracking, especially at elevate temperatures. Removal of process fluid is done at high temperatures, giving rise to extensive coking and plugging of removal apparatus. This effect is considered less for the feed injection because the feed stream is usually at lower temperatures.

Stage b: Determination of the optimal specie distribution

According to the Levenspiel (1999) the ideal flow regime for a A → B → C reaction scheme is plug flow. Thermal cracking is such a system, the primary cracking yields

the desired products, which is mono alkenes, and the secondary cracking is the further dehydrogenation of the desired product to di-alkenes, aromatics, etc.. We will investigate if we can draw the same conclusion with our *d*-RMix (1). In the previous paragraph, where we related the *d*-RMix to the attainable region theory, the reaction path is defined in concentration space. For a system with a small number of components this is useful because it is easy to visualize. We could determine the optimal mixing behavior for the same reason in composition space of ethane and ethene, since these are the most important. This is not possible when we consider the cracking of heavier feed stocks, because the reactant is not a single component. Therefore we selected, from an engineering point of view, the conversion-yield space. The conversion gives an indication on the separation effort, unreacted ethane is recycled back and the yield gives approximately the ethene yield of the plant. The conversion and yield are defined as follows

$$\xi = \frac{F_{C_2H_6,0} - F_{C_2H_6,V_t}}{F_{C_2H_6,0}} \tag{14}$$

$$Y = \frac{F_{C_2H_4,V_t}}{F_{C_2H_6,0}} \tag{15}$$

When dealing with heavier feed stocks, like for example naphtha's, gas oils and vacuum gas oils, the definition of the conversion, as given by (14), is not useable because the feed stock consist of a large number of components of which none is predominant. There are other conversion indicators available for these types of feed stocks as denoted by Golombok, M. et al. (2001). When heavier feed stocks are considered not only ethene is important for the yield, but nowadays propene is also important. Therefore a weighted sum of ethene and propene can be used as a yield function.

In order to get some insight into the conversion – yield space of the reaction system given in Table 1, we simulated the isothermal (and isobaric) cracking of ethane for several temperatures with a PFR model. The results are given in Figure 4. Each point in the figure is obtained by solving the PFR model with a given ethane inlet flow rate (*HC*, see Table 2), the *STOR* is kept the same (0.5). Again we selected arbitrarily 0.3 m³ as total reactor volume. The some numerical strategy was applied as mentioned earlier.
When we inspect the graphs in Figure 4 we see a clear maximum. The maximum values are reported in Table 3, these values are used for the explanation of the optimal temperature profiles in stage (*c*).

T [K]	ξ [−]	Y [mol·mol^{-1}]	HC [mol·s^{-1}]	τ [s]
1000	0.61	0.51	0.007	6.862
1100	0.85	0.74	0.070	0.629
1200	0.95	0.86	0.466	0.075
1300	0.98	0.91	2.915	0.011

Table 3: Conversion, C_2H_6 flow rate, residence time at maximum yield for different temperatures of Figure 4.
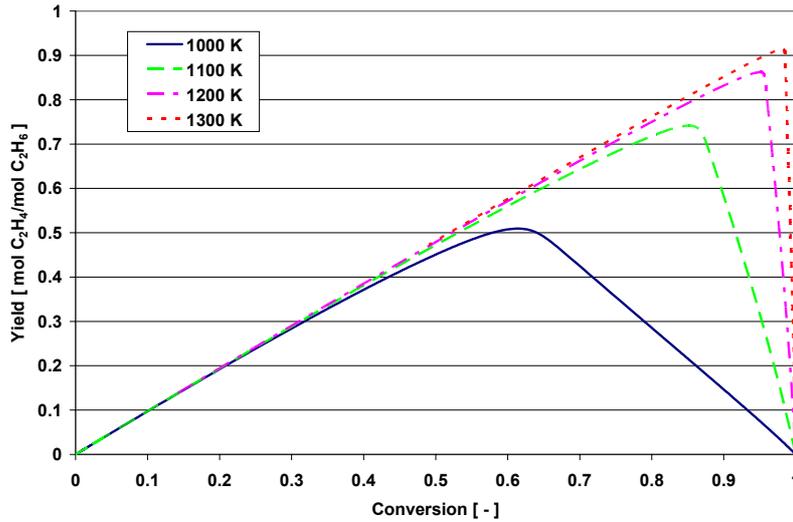
Figure 4 : PFR conversion - yield plots for the cracking of ethane at 1000, 1100, 1200 and 1300K at 1 bar.

In this stage we need to establish if the mixing and distribution of the feed injection can give higher yields than the isothermal/isobaric PFR value for a given conversion (residence time, feed flow rate). We address this question by solving an optimisation problem with the objective to maximise the yield, (15). The ethane flow rate, *HC*, is fixed for each optimisation. The free variables are the feed distribution function *L* and mixing kernel, *M*. We used between 5-10 sections to approximate *L* and *M* (= 30 − 110 free variables). We solved this optimisation problem for several values of *HC*, for 1100 and 1200 K the results are shown in Figure 5 and Figure 6. Similar results are obtained for 1000 and 1300 K, not shown in this paper.
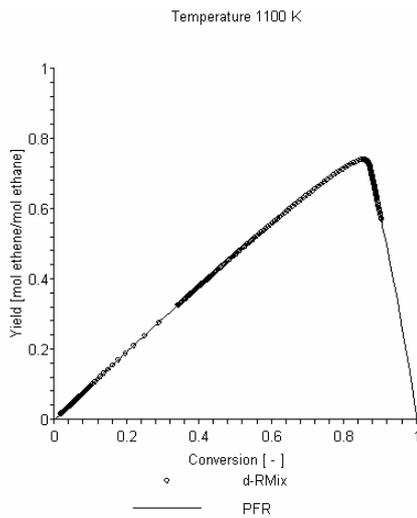
Figure 5: Optimal yield with *d*-RMix @ 1100 K   Figure 6: Optimal yield with *d*-RMix @ 1200 K
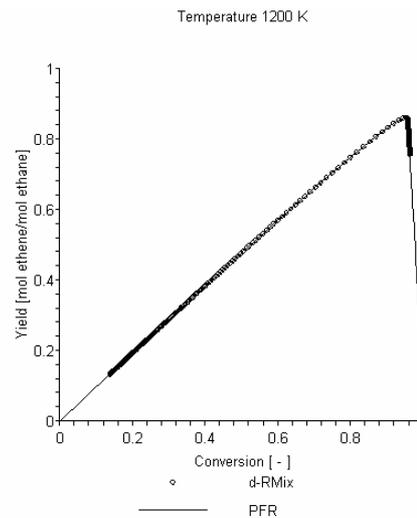
We conclude from Figure 5 and Figure 6 that no extension of the PFR profiles is obtained by mixing and/or distribution of the feed. The feed distribution function, *L*, is equal to the PFR model in all optimisations that is all the feed is added at the entrance of the reactor. The mixing kernel, *M*, is non-zero at high conversions where the yield is dropping. We can also from Figure 5 and Figure 6 observe that the yield of the *d*-RMix is equal to yield of the PFR. Therefore we can conclude that the PFR gives the optimal distribution of the species for isothermal and isobaric operation.

Stage c: Determination of the optimal temperature and pressure profiles

In the previous paragraph we have concluded that the PFR provides the optimal species distribution for the used kinetic scheme (Table 1). In this stage we determine what the optimal temperature and pressure profile is for this species distribution. If another temperature is obtained than isothermal we need to iterate between stage (*b*) and (*c*).

We used the same model as for stage (*b*) to determine the optimal temperature and pressure profiles. These optimal profiles are obtained by solving an optimisation problem with the objective to maximise the yield (15). The ethane flow rate, *HC*, is fixed for each optimisation. The free variables are the temperatures and pressures in the different sections. We used between 20-25 sections to approximate piecewise linear the temperature and pressure profiles. The pressure is forced to be larger than 1 bar by an inequality constraint. The temperature is forced to be larger than 600 K and smaller than some maximum temperature [1000, 1100, 1200, 1300 K]. At each maximum temperature we solved this problem for different values of the ethane feed flow rate *HC*. We observed that the isothermal and isobaric temperature profiles give the highest yield when the ethane feed rate *HC* was larger and equal then reported in Table 3 (the conversion and residence time are than smaller as reported in this table).
Profiles like given by Figure 7 are obtained when the *HC* value is smaller (residence time larger than reported in Table 3) than the values reported in Table 3. The resulting conversions, yields are equal to the values reported as can be seen from Table 4. The

residence time at the maximum temperature for Figure 7 is also given in Table 4. This value is similar to the one reported in Table 3. Therefore we can conclude that the optimal profile is isothermal at the maximum allowed temperature. Although we specify an ethane flow rate, *HC*, which will result in a larger residence time than the optimal one, the residence time at the maximum temperature will be equal to the optimal one. This gives equal optimal yields as reported in Table 3. The optimal pressure profiles are isobaric at 1 bar for all the optimisations.

Input			Results			
T_{min} [K]	T_{max} [K]	HC [mol·s^{-1}]	ξ [-]	Y [mol·mol^{-1}]	τ [s]	$\tau @ T_{max}$ [s]
600	1100	0.034	0.85	0.74	1.74	0.65

Table 4: Input and output values for the problem corresponding with Figure 7.
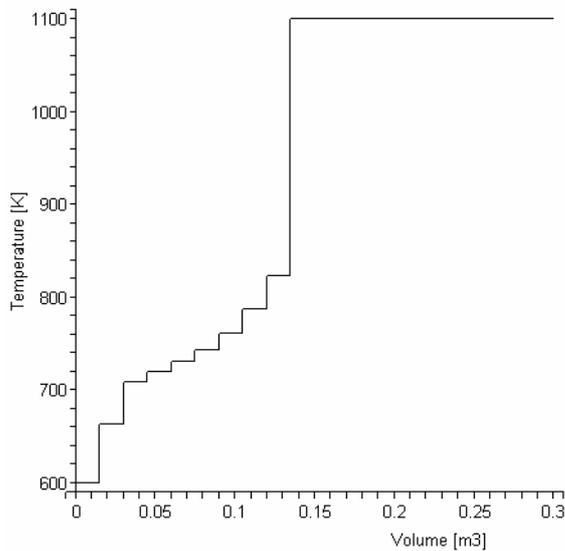
Figure 7 : Optimal temperature profile with maximum *T* of 1100 K and ethane feed rate of 0.034 mol·s^{-1}..

Conclusions

Synthesis of an one-dimensional reactor where convective transport and reaction, together with distributive feed injection, effluent removal and mixing, are considered, can be performed by means of a new continuous distributed species balance equation with differential and integral terms. The synthesis is accomplished through the introduction of three terms, representing a feed distribution function, an effluent removal function and a mixing kernel. Therefore we have called this approach the distributive reaction-mixing synthesis model, *d*-RMix. We have shown that the *d*-RMix embodies the ideal CSTR, PFR and DSR models.

The distributive functions and kernel are determined by optimisation to yield an optimal product yield under different constraints added by the designer. The translation of the resulting distributive policy into geometry for equipment is still under research.

We have demonstrated that the *d*-RMix is related to the attainable region theory. In the future the added value of this *d*-RMix approach needs to be proven.

We have applied the *d*-RMix to the thermal cracking of ethane. We extended the operation window in terms of maximum allowed temperature for future new or better materials to accommodate this process. On the basis of a small kinetic model we concluded that the PFR is the optimal specie distribution mode. It is also shown that isothermal and isobaric operation of the reactor at the maximum allowed temperature and lowest allowed pressure is the most optimal one.

Acknowledgements

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Appendix A : Derivation of the *d*-RMix

In this appendix the *d*-RMix and its constraints are derived. Consider a series of equally sized CSTRs, as shown by Figure 8. There is a net flow of material from the entrance to the exit. On top of this flow all the CSTRs can exchange material with one another and product can be removed from all these CSTRs.
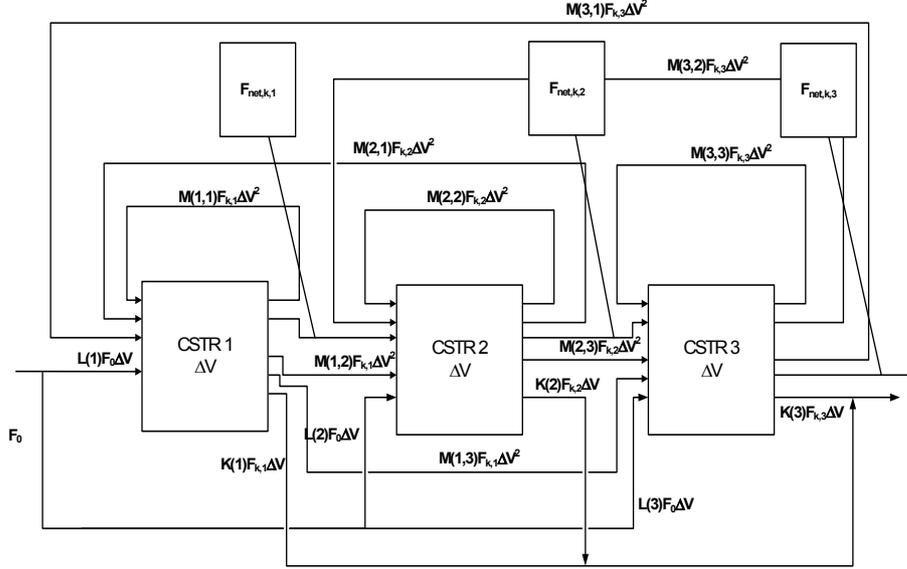
Figure 8: Schematic of the *d*-RMix principle for 3 interconnected CSTR's.

The kth component balance of the ith CSTR is given by:

$$\frac{\partial C_{k,i/N}\Delta V}{\partial t} = F_{net,k,(i-1)/N} - F_{net,k,i/N} + R_{k,i/N}\Delta V + L\left(i/N\right)F0_k\Delta V \; -$$

$$K\left(i/N\right)F_{k,i/N}\Delta V + \Delta V\sum_{j=1}^{N}F_{k,j/N}M\left(j/N,i/N\right)\Delta V \; - \qquad (16)$$

$$\Delta V\sum_{j=1}^{N}F_{k,i/N}M\left(i/N,j/N\right)\Delta V$$

When we let the number of CSTR's go to infinity, the following differential-integral equation (1) is obtained:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} + L\left(V\right)F0_k - K\left(V\right)F_{k,V} +$$

$$\int_{0}^{V_t}\left(F_{k,v}M\left(v,V\right) - F_{k,V}M\left(V,v\right)\right)dv \qquad (17)$$

The feed distribution, and product removal functions and mixing kernel: *L, K, M,* are independent of the species and subject to physical feasibility constraints, like non-negative flows in the system:

$$L\left(v\right) \geq 0 \qquad v \in \left[0,V_t\right] \qquad (18)$$

$$M(v,v) \geq 0 \quad v \in [0,V_t] \tag{19}$$

$$K(v) \geq 0 \quad v \in [0,V_t] \tag{20}$$

All the available feed should be released in side (and/or by pass) the reactor:

$$\int_0^{V_t} L(v)\,dv = 1 \tag{21}$$

In the distributive reaction-mixing equation (17) we have two molar flow rates namely the total flow rate and the net molar flow rate. The total flow rate is the sum of the net flow rate, the amount mixed away and the amount removed from the volume element. This is defined by the following equation:

$$F_{k,\mu} = F_{net,k,\mu} + \int_0^{V_t} F_{k,\mu}\delta(v-\mu)h(v)\,dv +$$
$$\int_0^{V_t} F_{k,\mu}\delta(v-\mu)K(v)\,dv \quad \mu \in [0,V_t] \tag{22}$$

Or rewritten as

$$F_{net,k,\mu} = F_{k,\mu}\left(1 - \int_0^{V_t}\delta(v-\mu)h(v)\,dv - \int_0^{V_t}\delta(v-\mu)K(v)\,dv\right) \quad \mu \in [0,V_t] \tag{23}$$

The function h, used in equation (22) and (23), defines the fraction of the total flow mixed away:

$$h(\mu) = \int_0^{V_t} M(\mu,v)\,dv \quad \mu \in [0,V_t] \tag{24}$$

From equation (23) it will be clear that we need to impose the following constraint in order to obtain positive and non-zero flow rates.

$$\int_0^{V_t}\delta(v-\mu)h(v)\,dv + \int_0^{V_t}\delta(v-\mu)K(v)\,dv < 1 \quad \mu \in [0,V_t] \tag{25}$$

The mixing kernel, *M*, cannot contribute to the overall production of a component in the total reaction volume, only locally, therefore the mixing kernel should fulfil the following constraint:

$$\int_0^{V_t}\int_0^{V_t} M(v,V)\,dv\,dV = \int_0^{V_t}\int_0^{V_t} M(V,v)\,dv\,dV \tag{26}$$

The final item that must be defined is the boundary value for the net flow rate, this is given by the following equation:

$$F_{net,k,0} = \int_0^{V_t}\delta(v)L(v)F0_k\,dv \tag{27}$$

Appendix B: Distributive reaction-mixing model – Ideal Reactors

PFR

The distributive reaction-mixing model equation (1) embodies the PFR, DSR and CSTR models as special cases. First we will show how the PFR results are obtained. We define the following feed injection function, mixing kernel and extraction functions (L, M, K):

$$L(v) = \begin{cases} 1 & 0 \\ 0 & else \end{cases}$$

$$M(v,\mu) = Mm\,\delta(v-\mu) \qquad Mm \geq 0$$

$$K(v) = 0$$

We only add feed at the entrance of the reactor and extract no fluid along the reactor coordinate. We allow only mixing towards and from the same location. Substitution of the functions, kernel L, K, M gives ($V > 0$):

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} + \int_0^{V_t} Mm\,\delta(v-V)\left(F_{k,v} - F_{k,V}\right)dv \qquad (28)$$

The boundary equation (27) changed to

$$F_{net,k,0} = \int_0^{V_t} \delta(v)L(0)F0_k\,dv = F0_k \qquad (29)$$

The integral in equation (28) can be evaluated, yielding the standard equation for the description of the PFR:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} \qquad F_{net,k,0} = F0_k \qquad (30)$$

DSR

The DSR model is derived in a similar fashion as for the PFR, where the feed and product removal functions, L, K, are defined as non-zero functions for the whole or part of the reaction coordinate V.

CSTR

For the CSTR model we define that the feed is only injected at the entrance of the reactor, no fluid is removed along the reactor coordinate and a constant mixing rate is applied. This is defined by the following equations:

$$L(v) = \begin{cases} 1 & 0 \\ 0 & else \end{cases}$$

$$M(v,\mu) = \frac{Mm}{V_t} \qquad 0 \leq Mm < 1$$

$$K(v) = 0$$

The boundary equation (27) changed to

$$F_{net,k,0} = \int_0^{V_t} \delta(v) L(0) F0_k \, dv = F0_k \tag{31}$$

Substitution of the functions, kernel L, K, M gives ($V > 0$) the following equation:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} + \frac{Mm}{V_t} \int_0^{V_t} \left(F_{k,v} - F_{k,V} \right) dv \tag{32}$$

The relation between de total molar flow rate and the net molar flow rate is defined by (22), when we substitute the two functions and kernel we obtain the following relation:

$$F_{net,k,\mu} = F_{k,\mu} \left(1 - \int_0^{V_t} \delta(v - \mu) Mm \, dv \right) = F_{k,\mu}(1 - Mm) \quad \mu \in [0, V_t] \tag{33}$$

The model equation that describes the CSTR model is obtained by the elimination of the total molar flow rate with (33):

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + R_{k,V} + \frac{Mm}{(1-Mm)V_t} \int_0^{V_t} \left(F_{net,k,v} - F_{net,k,V} \right) dv \tag{34}$$

When the mixing rate is high ($Mm \sim 1$) the gradient of the flow will be zero except where the feed enters the reaction volume; there an almost infinite gradient will be observed. Figure 9 gives an indication how the profiles look like to model a CSTR with the d-RMix. These profiles are for reaction scheme (2), an exit concentration of A of 0.3 mol·m^3, and a mixing constant Mm of 0.99.
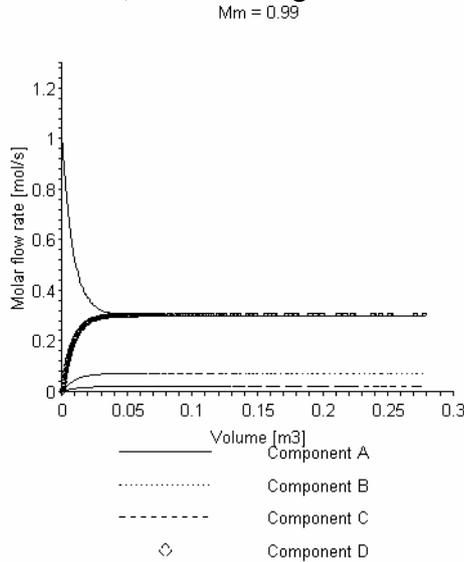
Figure 9: Typical d-RMix profiles for a CSTR with a mixing constant of 0.99, exit concentration of A is 0.3 mol·m^3.