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# PROJECT – STEAMCRACKER PLUG FLOW REACTOR CRACKING NAPHTHA

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## **Abstract**

Steamcracking is one of the largest processes in petrochemical industry. The principal feedstock is naphtha generated of crude oil and gas. Naphtha consists of several long chained hydrocarbons, whose C-C and C-H bonds are broken to gain alkenes.

Due to the variety of hydrocarbones in the feed, there is a big reaction network with many decomposition and temporary reactions. Because of the complexity of the network with different time scales and the weight of each reaction in the scheme an implementation is quite complicated.

The aim of this work was to create a mathematical model for a PFTR and run corresponding simulations in MATLAB ®. Based on the model equations different process parameters were optimized to reach a maximum alken mass fraction with the least effort of raw product.

With the implemented reaction scheme we achieved results describing the main behavior of an industrial steamcracker. It was possible to find optimal process parameters.

# Chapter 1

## Introduction

### 1.1 Theory of thermal cracking

In the 1920s there was a change in the US petrochemical industry. Due to the lavishness of the ethine chemistry it was necessary to build an industry based on cheaper routes. This was the cause of the development of ethene based industry. Because of the rise of automotive industry there was an incredible demand for gasoline. So they invented new cracking plants for optimal raw fuel cracking where alkenes appeared as byproduct. When the ethene demand increased they needed it no longer as by- but as a main product. So the steamcracker was designed.

In a steamcracker liquid hydrocarbons are cracked into short-chained hydrocarbons using temperatures between 800 and 850 degrees of Celsius. Before cracking the naphtha is diluted with steam to avoid polymerization of the interstages or breakup of hydrocarbon molecules. The steamcracking of naphtha produces ethene and propene in a 2 to 1 ratio. As byproducts there are hydrogen, methane and  $C_4$ - and  $C_5+$ -hydrocarbons. At the heat reduction of cracking products a lot of high pressure vapor is generated, which is used as an energy supply. In crude oil and gas there is only a small fraction of alkenes. They need to be produced by special cracking processes. During steamcracking at first the C-C bonds are broken up which leads to a formation of radicals, the educts of subsequent reactions. These subsequent reactions form stable products only after a plenty of intermediate reaction steps.

Larger molecules cause many decomposition- and temporary reactions. Hence, there are over one hundred different components in the mixture. As side reactions there are isomerisations, cyclizations and aromatizations. One can make some assumptions based on chemistry and thermodynamics of hydrocarbons:

- short chained molecules are more stable than long chained
- saturated hydrocarbons are less stable than unsaturated at temperatures above 500 degrees of Celsius
- cyclo-alkenes are closer to the alkene attitude than aromatic hydrocarbons
- hydrocarbon aromatics are most stable
- C-C-bonds can be cracked most easily, followed by C-H-alkene-bonds and after this two C-H-cyclo-alkene bonds

Cracking the hydrocarbons until the thermodynamical equilibrium one will only get pure hydrogen and carbon as elements. If one wants to get an optimal yield of ethene and propene it will be necessary to transfer a large amount of energy in very small time. Otherwise one gets unrequested side or subsequent reactions. Four conditions are important for a good result:

1. kind of used hydrocarbons

- the more complex the molecules, the more hydrogen and methane is generated (n-alkenes better than i-alkenes)
- ethene yield is decreasing in the following order:  
n-alkenes  $\gg$  cyclo-alkenes  $\approx$  i-alkenes  $>$  aromatic hydrocarbons

- thermal cracking of n-alkenes leads to lots of usable byproducts
2. cracking temperature
    - industry uses cracking temperatures between 700 and 900 degrees of celcius for maximal alkene yield
    - maximal alkene and propene yield is reached at temperatures between 800 and 850 degrees of celcius
  3. retention time
    - short retention times cause desired alkenes through primary reactions
    - longer retention times cause side reactions and valuable products
  4. partial pressures of hydrocarbons
    - thermal decomposition is benefited by low partial pressure (Le Chatelier-Brown)
    - mixing pyrolysis gas with steam also decreases the partial pressure

## 1.2 Technical procedure

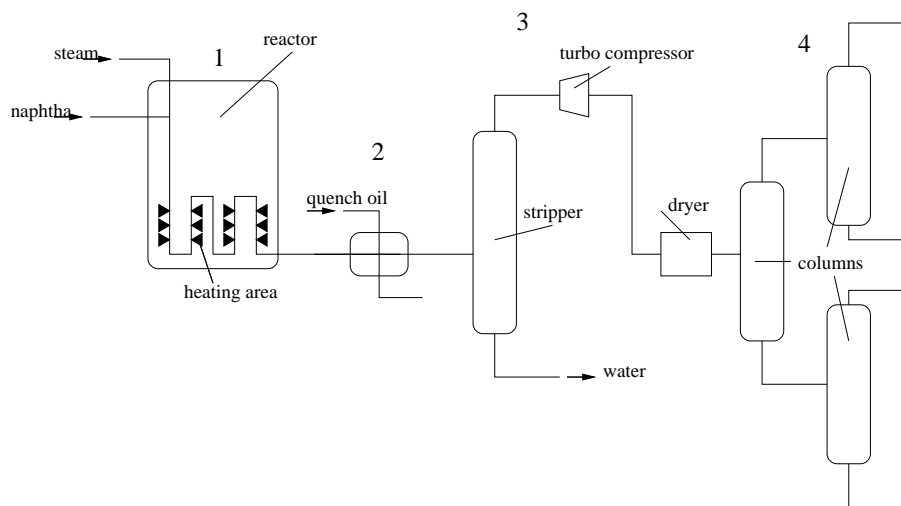


Figure 1.1: Steamcracker schema

As mapped on figure 1.1 there are four steps needed for steamcracking

1. cracking naphtha in the cracking furnaces

- short residence time (<0.5s)
- vaporized naphtha is mixed with steam
- mixture heated up to 600 degrees of celcius
- in pipes with length of 20 to 70 m and width of 40 to 100 mm mixture is heated up to 840 degrees of celcius

2. quencher

- gas velocity 200 - 300 m/s
- temperature reduced to 400 degrees of celcius
- with oil injection down to 200 degrees of celcius
- avoids recombination of short-chained hydrocarbons
- heat of downcooling produces overheated steam for cracking

3. compression and purification

- due to cooling down there is some hydrocarbonic condensate in the condensed process water
- in a stripping column process water is cleared from organic components
- in a 5 step turbocompressor the gas is compressed from 1.3 bar up to 32 bar
- after every stage the mixture is cooled down to maximal 95 degrees of celcius to avoid polymerization
- between the 4th and the 5th stage carbondioxid and hydrogen sulfide are washed out by using a soda lye

4. drying, cooling, distillation

- water removing by cooling down to -60 degree of celcius over molar filter
- in several deep temperature (down to -160 degree of celcius) columns the raw gas is decomposed in several fractions
- $C_{2-}/C_{3+}$  splitter, where ethene, hydrogen, methane and ethane is extracted from the  $C_2$  fraction
- $C_3/C_4$  splitter, where propane, propylene, alkene and alkylene is extracted from the  $C_3$  fraction
- $C_4/C_5$  splitter where the  $C_4$  fraction is splitted from the mixture
- the pygas from the  $C_5$  is hydrogenated and fractionated to get fuels and aromatic hydrocarbons

## Chapter 2

### Derivation of the balances

When we look at a typical reactor, which is used for steam cracking, we can make different assumptions to find a mathematical model, which can be simulated easily. There are balances for the total energy, the total and component mass and the momentum of a system. In the following part we discuss the different model assumptions and simplify each balance.

#### 2.1 Assumptions

1. The reactor is a very long tube. So the diameter is much smaller than the length and one can neglect radial gradients.
2. The velocity of the inner components is very high because of a short retention time.

$$v \approx \frac{\bar{L}}{\bar{\tau}} \approx \frac{70m}{0,3s} \approx 233,33m/s \quad (2.1)$$

3. The molar mass of each component is constant.
4. The reactor is a round tube so one has rotational symmetry around the axis.
5. The velocity is very high, so one can neglect small changes. The velocity is nearly constant.
6. One can describe the cooling of the reactor by an easy driving force law. (heat conduction between two parallel walls)

#### 2.2 Derivation of the total mass balance

First, we have to set up a mass balance for a small part of the tube ( $dz \rightarrow 0$ ). We look at the changing of  $d\mathbf{m}$ , shown in figure 2.1.

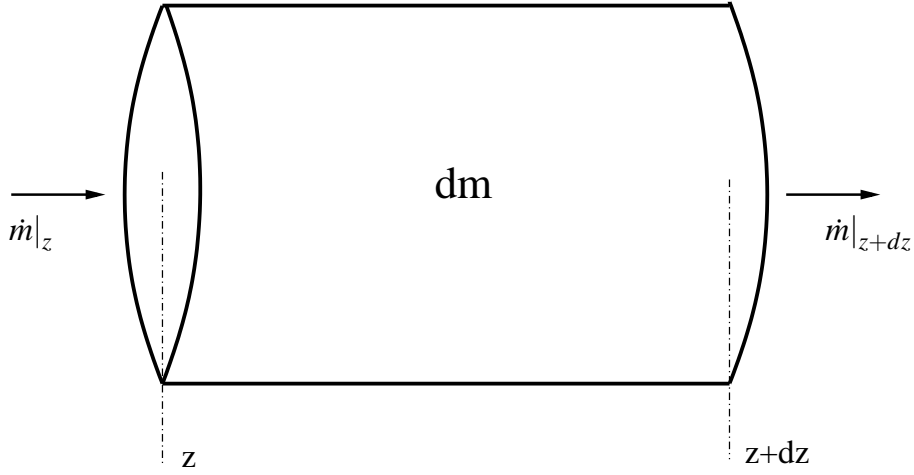


Figure 2.1: Part of the tube

$$\frac{\partial}{\partial t}(d\mathbf{m}) = \frac{\partial}{\partial t} \left( \underbrace{Adz}_{=V} \frac{\mathbf{n} \mathbf{m}}{V \mathbf{n}} \right) \quad (2.2)$$

$$= \frac{\partial}{\partial t} (Adz \mathbf{c} \tilde{\mathbf{M}}) \quad (2.3)$$

$$= \dot{\mathbf{m}}|_{\mathbf{x}} - \dot{\mathbf{m}}|_{\mathbf{x}+d\mathbf{x}} + \dot{\mathbf{m}}_a^* \frac{A}{l} d\mathbf{z} + \boldsymbol{\sigma} \cdot A d\mathbf{z} \quad (2.4)$$

Taylor series of  $\dot{\mathbf{m}}$ :

$$\dot{\mathbf{m}}|_{\mathbf{x}+d\mathbf{x}} = \dot{\mathbf{m}}|_{\mathbf{x}} + \left. \frac{\partial \dot{\mathbf{m}}}{\partial \mathbf{z}} \right|_{\mathbf{x}} d\mathbf{z} + \dots \quad (2.5)$$

$$A \tilde{\mathbf{M}} \frac{\partial \mathbf{c}}{\partial t} d\mathbf{z} = - \frac{\partial \dot{\mathbf{m}}}{\partial \mathbf{z}} d\mathbf{z} + \boldsymbol{\sigma} A d\mathbf{z} \quad (2.6)$$

$$A \tilde{\mathbf{M}} \frac{\partial \mathbf{c}}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} (\dot{\mathbf{m}}_C + \dot{\mathbf{m}}_D) + \boldsymbol{\sigma} A \quad (2.7)$$

$$A \tilde{\mathbf{M}} \frac{\partial \mathbf{c}}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} (\dot{V} \tilde{\mathbf{M}} \mathbf{c} + \dot{\mathbf{m}}_D) + \boldsymbol{\sigma} A \quad (2.8)$$

We can use assumptions [A1] and [A2] to neglect the diffusion in the tube (no radial gradients and dominance of convection in contrast to diffusion).

$$\frac{\partial \rho}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} (\mathbf{v} \rho) + \sigma \quad (2.9)$$

$$\frac{\partial \mathbf{c}}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} (\mathbf{v} \mathbf{c}) + \frac{\boldsymbol{\sigma}}{\tilde{\mathbf{M}}} \quad (2.10)$$

If we look at the total mass balance by summing up

$$\sum_i^N \frac{\partial \rho_i}{\partial t}$$

the source term drops out.

$$\frac{\partial \rho}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} (\rho \mathbf{v}) \quad (2.11)$$

$\mathbf{m}$	...	mass
$\tilde{\mathbf{M}}$	...	molar mass
$\dot{\mathbf{m}}$	...	mass flow
$\mathbf{c}$	...	molar concentration
$\dot{\mathbf{m}}_a^*$	...	mass flow (area specific)
$\dot{\mathbf{m}}_C$	...	mass flow(convection)
$\dot{\mathbf{m}}_D$	...	mass flow(diffusion)
$\sigma$	...	sink/source
$\rho$	...	density
$\dot{V}$	...	volume flow
$\mathbf{z} \in \mathbb{R}^3$	...	spacial coordinates
$\rho$	...	total mean density of all components
$\mathbf{v} \in \mathbb{R}^3$	...	velocity vector and
$t$	...	time

Now we use cylindric coordinates for a singular transformation of this partial differential equation:

$$\mathbf{z} = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} = \begin{pmatrix} r \cos(\Theta) \\ r \sin(\Theta) \\ z \end{pmatrix} \Leftrightarrow \mathbf{x} = \begin{pmatrix} r \\ \Theta \\ z \end{pmatrix} = \begin{pmatrix} \sqrt{z_1^2 + z_2^2} \\ \arctan\left(\frac{z_1}{z_2}\right) \\ z_3 \end{pmatrix} \quad (2.12)$$

The transformation does not change the accumulation term on the left hand side, but the derivative of the vector  $\mathbf{v}$  w.r.t.  $\mathbf{z}$ .

$$\frac{\partial \mathbf{v}}{\partial \mathbf{z}} = \nabla_x \mathbf{v} = \frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial v_\Theta}{\partial \Theta} + \frac{\partial v_z}{\partial z} \quad (2.13)$$

But the system is rotationally symmetric [A4] and the diameter is much smaller than the length [A1].

$$\frac{\partial}{\partial \Theta} = 0, \frac{\partial}{\partial r} = 0 \quad (2.14)$$

When we look at assumption [A5] the derivative of the velocity is zero anyway and equation (2.11) changes to:

$$\frac{\partial \rho}{\partial t} = -v_z \frac{\partial \rho}{\partial z} \quad (2.15)$$

In the following  $v_z$  is defined as  $v$ . The mean density is a summation of the partial densities of the components  $\alpha$  and it depends on the molar mass and the concentration.

$$\sum_{\alpha} \rho_{\alpha} = \sum_{\alpha} M_{\alpha} c_{\alpha} = \bar{M} \sum_{\alpha} c_{\alpha} \quad (2.16)$$

Now one can substitute this in equation (2.15) and divide by a constant [3] mean molar mass and one has the total mass balance (TMB):

$$\frac{\partial \sum_{\alpha} c_{\alpha}}{\partial t} = -v \frac{\partial \sum_{\alpha} c_{\alpha}}{\partial z} \quad (2.17)$$

### 2.3 Derivation of the component mass balances

We will start with the local partial mass balance for one component  $\alpha$  in Cartesian coordinates (eq.(2.9)).

$$\frac{\partial \rho_\alpha}{\partial t} = -\frac{\partial}{\partial \mathbf{z}} (\rho_\alpha \mathbf{v}) + \sigma_\alpha \quad (2.18)$$

$\mathbf{j}_\alpha$  ... diffusion term of component  $\alpha$  in each direction  
 $\sigma_\alpha$  ... source/sink of component  $\alpha$

We reduce the coordinates as before and factor out the velocity (=const.). With equation (2.16) we obtain the mass balance for component  $\alpha$  (CMB):

$$\frac{\partial c_\alpha}{\partial t} = -v \frac{\partial c_\alpha}{\partial z} + \frac{1}{M_\alpha} \sigma_\alpha \quad (2.19)$$

The last term on the right hand side is the molar source/sink of component  $\alpha$  effected by reaction (i.a. modeling of reaction kinetics in the following).

Sometimes it is easier to implement the system by using mass fractions  $w$  instead of concentrations.

$$\begin{aligned} c_\alpha &= \frac{n}{V} \\ &= \frac{m_\alpha}{V \bar{M}} \\ &= \frac{m_\alpha}{V \bar{M}} \frac{m}{m} \\ &= \frac{\rho}{\bar{M}} w \end{aligned}$$

### 2.4 Derivation of the energy balance

We will start with the local total energy balance in temperature mode:

$$\underbrace{\rho c_P \frac{\partial T}{\partial t}}_{L1} + \underbrace{\left[ \rho \left( \frac{\partial h}{\partial p} \right)_{w_\alpha, T} - 1 \right] \left( \frac{\partial p}{\partial t} + \mathbf{v} \frac{\partial p}{\partial \mathbf{z}} \right)}_{L2} = \underbrace{-\sum_\alpha h_\alpha \sigma_\alpha}_{R1} - \underbrace{\frac{\partial \mathbf{q}}{\partial \mathbf{z}}}_{R2} - \underbrace{\rho c_P \mathbf{v} \frac{\partial T}{\partial \mathbf{z}}}_{R3} + \underbrace{\sum_\alpha \mathbf{j}_\alpha \left( \mathbf{f}_\alpha - \frac{\partial h_\alpha}{\partial \mathbf{z}} \right)}_{R4} - \underbrace{\pi \frac{\partial \mathbf{v}}{\partial \mathbf{z}}}_{R5} \quad (2.20)$$

L1 accumulation of enthalpy  
 L2 pressure influence  
 R1 energyinput by reaction  
 R2 heatflow over the system-boundaries  
 R3 energyflow by convection  
 R4 effects of diffusion  
 R5 effects of friction

We do not have the assumption that the pressure is constant, but the derivative of enthalpy on constant temperature and mass fraction can be neglected. There are no effects of diffusion (R4) (i.a. [A1] and [A2]) and the friction is neglected by the same reasons. After a reduction of coordinates (see above) the equation is very short:

$$\rho c_P \frac{\partial T}{\partial t} - 1 \left( \frac{\partial p}{\partial t} + v \frac{\partial p}{\partial z} \right) = -\sum_\alpha h_\alpha \sigma_\alpha - \frac{\partial \mathbf{q}}{\partial z} - \rho c_P v \frac{\partial T}{\partial z} \quad (2.21)$$

Now we use again equation (2.16) and divide the last equation by a constant mean molar mass.

$$\sum_{\alpha} c_{\alpha} c_{P,\alpha} \frac{\partial T}{\partial t} - \frac{1}{M} \left( \frac{\partial p}{\partial t} + v \frac{\partial p}{\partial z} \right) = - \sum_{\alpha} h_{\alpha} \sigma_{\alpha}^{molar} - \frac{\partial \mathbf{q}^{molar}}{\partial z} - \sum_{\alpha} c_{\alpha} c_{P,\alpha} v \frac{\partial T}{\partial z} \quad (2.22)$$

Some variables are molar. From now on we use  $\sim$  to describe the reference to the molar mass. For the energy input by reaction (R1) and the heatflow over the system-boundaries (R2) one can take the following approaches [A6]:

$$- \sum_{\alpha} h_{\alpha} \tilde{\sigma}_{\alpha} = \sum_m^R (-\Delta \tilde{H}_R)_m \tilde{r}_m(c_{\alpha}, T) \quad (2.23)$$

$$- \frac{\partial \tilde{\mathbf{q}}}{\partial z} = k_W A_W (T_W - T) \quad (2.24)$$

Calculations of the reaction rate  $r_m$  and the heat of reaction  $(-\Delta \tilde{H}_R)_m$  will follow in the part modeling of reaction kinetics. The total energy balance (TEB) results in:

$$\left( \sum_{\alpha} c_{\alpha} c_{P,\alpha} \right) \frac{\partial T}{\partial t} - \frac{1}{M} \left( \frac{\partial p}{\partial t} + v \frac{\partial p}{\partial z} \right) = \sum_m^R (-\Delta \tilde{H}_R)_m \tilde{r}_m(c_{\alpha}, T) + k_W A_W (T_W - T) - v \left( \sum_{\alpha} c_{\alpha} c_{P,\alpha} \right) \frac{\partial T}{\partial z} \quad (2.25)$$

$R$	...	number of reactions
$c_{P,\alpha}$	...	heat capacity of component $\alpha$
$(-\Delta \tilde{H}_R)_m$	...	heat of reaction $m$
$\tilde{r}(c_{\alpha}, T)$	...	molar reaction rate
$k_W$	...	coefficient for heat transfer
$A_W$	...	area for heat transfer
$T_W$	...	temperature of the heating/cooling tube wall

## 2.5 Heuristic estimation of pressure drop <sup>1</sup>

The velocity is constant, so one needs no momentum balance. But for the estimation of the pressure drop (PD) there is an equation depending on the friction factor and the local resistance coefficient:

$$\frac{dp}{dz} = \left( f \frac{L}{144dg} + \xi(z) \right) \frac{\rho v^2}{2} \quad (2.26)$$

The derivative of the pressure is written in the substantial mode. But when one uses the relation between the Lagrangian and the Eulerien views of fluid motion one can convert the left hand side of the equation and substitute the pressure drop in the energy balance.

$$\frac{dp}{dz} = \frac{\partial p}{\partial t} + v \frac{\partial p}{\partial z} \quad (2.27)$$

The friction factor in equation (2.26) is for hydraulic smooth tubes:

$$f = 0.3164 Re^{-0.25} \quad (2.28)$$

With the Reynolds number:

$$Re = \frac{dv}{\eta} \quad (2.29)$$

$d$	...	diameter of the tube reactor
$\eta$	...	dynamic viscosity of the inner fluid
$\xi(z)$	...	local resistance coefficient depending on $z$
$g$	...	gravity constant

<sup>1</sup>Pressure drop is not implemented in the MATLAB®

## 2.6 Modeling of reaction kinetics

For modelling the kinetic mechanism of a steamcracker one needs a network of chemical reaction (Appendix A) with different parameters for the description of reaction rates and heat of reaction. The chemical reactions act like a source/sink of the amount of substance in the CMB and of chemical energy in the TEB. The term  $\sigma_\alpha$  can be written like this:

$$\frac{1}{M}\sigma_\alpha = \widetilde{\sigma}_\alpha = \sum_m^R v_m \widetilde{r}_m(c_\alpha, T) \quad (2.30)$$

Here one has to sum up all reaction rates (reactions containing  $\alpha$ ) multiplied by the stoichiometric factor  $v$ . For the reaction rates one can use a power law:

$$r_m(c_\alpha, T) = \widetilde{k}_m(T) \prod_{i \in E_d}^{N_{E_d}} c_{m,i}^{|v_{i,E_d}|} \quad (2.31)$$

With a temperature depending constant  $\widetilde{k}_m$  and the product of the educt concentrations to the power of their stoichiometric factors. For the temperature depending constant applies the Arrhenius equation:

$$\widetilde{k}_m = \widetilde{k}_{\infty,m} \exp\left(\frac{-E_{A,m}}{RT}\right) \quad (2.32)$$

With the activation energy of each reaction and a constant  $\widetilde{k}_{\infty,m}$ .  $T$  and  $R$  are the temperature and the universal gas constant. The enthalpy of reaction  $(-\Delta\widetilde{H}_R)_m$  of each reaction can be formulated as the sum of the enthalpy of formation of each component attending the reaction (l.a.TEB):

$$(-\Delta\widetilde{H}_R)_m = \left( \sum_i^{C_R} v_i (\Delta\widetilde{H}_F)_i \right)_m \quad (2.33)$$

## 2.7 Equations for steady state simulations

We will simulate the steamcracker model at a steady state. This means that the derivatives with respect to time  $t$  will cancel out.

$$\frac{\partial}{\partial t} (\cdot) \stackrel{!}{=} 0 \quad (2.34)$$

**Set of equations** used for the simulation:

Component mass balance (2.19)

$$\frac{\partial w_\alpha}{\partial z} = \frac{1}{v\rho} \sigma_\alpha \quad (2.35)$$

Energy balance (2.25)

$$\frac{\partial T}{\partial z} = \frac{1}{v(\sum_\alpha c_\alpha c_P)} \left[ \sum_m^R (-\Delta\widetilde{H}_R)_m \widetilde{r}_m(c_\alpha, T) + k_W A_W (T_W - T) \right] \quad (2.36)$$

## Chapter 3

### Implementation in MATLAB®

To implement the ordinary differential equations a numerical tool must be used. For this we take MATLAB® and follow basically this steps:

- control parameters for the script
- definition of the system parameters
- call some matrices for getting parameters
- set boundary and initial conditions
- calling an ODE-solver for stiff ODE systems
- analysis

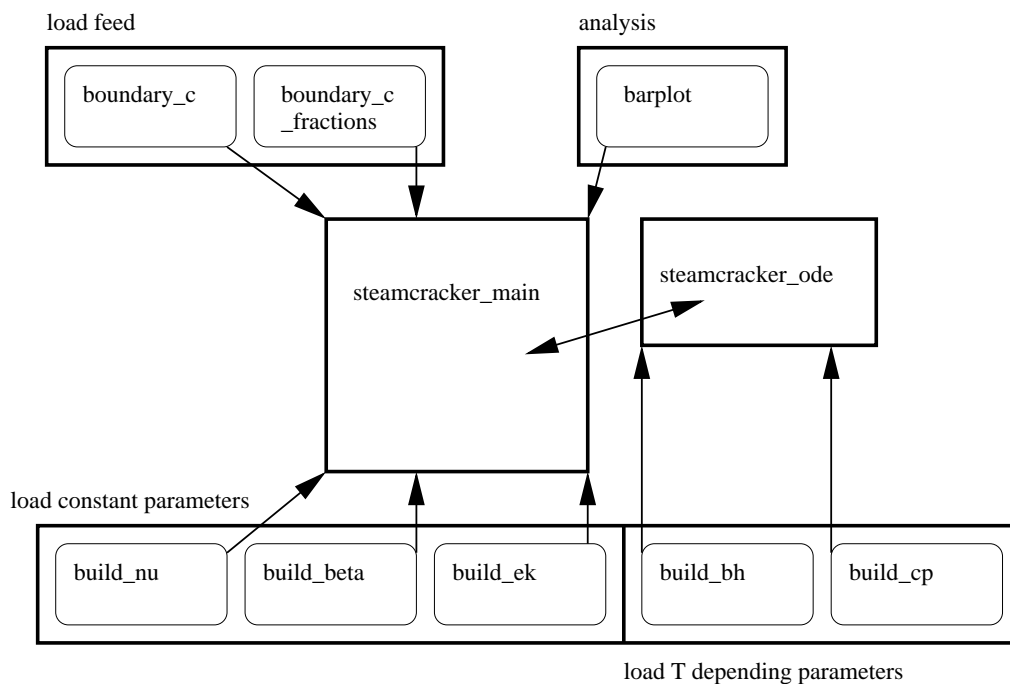


Figure 3.1: Overview of Functions

#### 3.1 Control parameters for the script

To make the script more flexible we implemented different possibilities:

- choose two different defined or in C-fractions partitioned feeds

- choose operational mode of the reactor (isotherm, adiabat, with heating)
- choose operational parameters for variation (e.g.  $T$ ,  $\tau$  and  $x_{steam}$ )
- choose different plots for analysis

For individual parameter studies the script can be modified easily. Therefor one can start the steamcracker function and vary each parameter successively to produce a parameterplot for interesting values (e.g. yield of  $C_2$ -fraction).

## 3.2 Definition of the system parameters

The system parameters involve reaction parameters (represented by a matrix of stoichiometric coefficients and kinetic constants), geometric and thermodynamic parameters. As thermodynamic parameters there are defined substance values for the hydrocarbons (e.g. molar masses, heat capacities and standard enthalpies of formation) and variable operating conditions (e.g. inlet temperature or wall temperature). The substance values can be temperature depending. And as geometric parameters for example the tube diameter or length.

### Call some matrices for getting parameters

- implement the  $\nu$ -matrix (stoichiometric factors of all reactions for the components)
- implement the  $\beta$ -matrix (quantity of Elements H,C and O for each component)
- implement the  $ek$ -matrix (Matrix of kinetic constants for each reaction)
- implement the  $bh$ -matrix (Matrix for standard formation enthalpies) and calculate reaction enthalpies

**Additional tools for testing reaction scheme** In our first simulations we reduced the reaction scheme by clearing the  $\nu$ -matrix in a specified range. An other approach to check the rightness of the reaction scheme was to control the conservation of mass for each reaction (i.e. the number of elements on the right and left hand side)

## 3.3 Set boundary and initial conditions

Corresponding to the choosen feed the mass fractions are assigned. Besides the inlet temperature has to be set. In the isothermic case the inlet temperature is the allover tube temperature (it has to be high enough to start the reactions). In the non isothermic case the inlet temperature is lower, because here the allover temperature is more or less controled by the wall temperature.

## 3.4 Calling the ODE-solver

We combine the BCs in one vector and call an appropriate ODE-solver for an interval  $z \in [0, L]$ . Because of the different time scaling of the reactions an ODE-solver for stiff equations is required.

## 3.5 Analysis

For analysis the script offers different plots:

- simulation of a bar chart as a video application, showing the chain lengths over  $z$
- plot the mean chain length over  $z$

- plot temperature over  $z$
- plot error (sum of all mass fractions) over  $z$
- plot 3D-bar of mass fractions over  $z$
- plot  $C_1$ -,  $C_2$ - and  $C_3$ -fractions over  $z$

### 3.6 ODE function

We call the ODE-function `steamcracker_ode`. As input variables it gets the position  $z$ , the time and parameters. The output vector contains the derivation of temperature for the energy balance and all derivations of mass fractions for each component.

Consider following steps:

- compute source/sink-term with reaction rates and Arrhenius approach
- compute vector of derivations of mass fractions (use molar mass vector and source/sink term)
- compute terms of energy balance (get  $c_p$ - and  $E_f$ -values from the corresponding function of T)
- compute derivation of temperature by using this terms

## Chapter 4

# Parameter studies and simulation results

### 4.1 Model validation

To check the accuracy and rightness of our model and the simulations we plotted the sum of all mass fractions over the tube length and compared the output mass fractions for the different C-fractions with experimental results [DR83]:

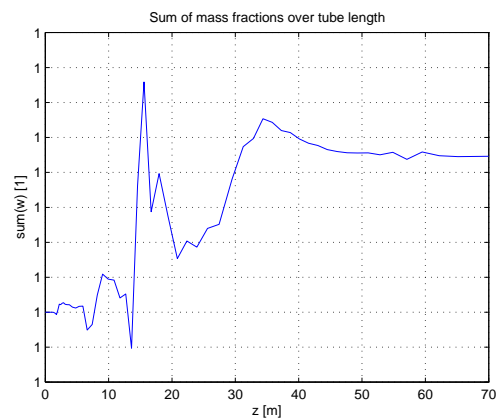


Figure 4.1: Error plot

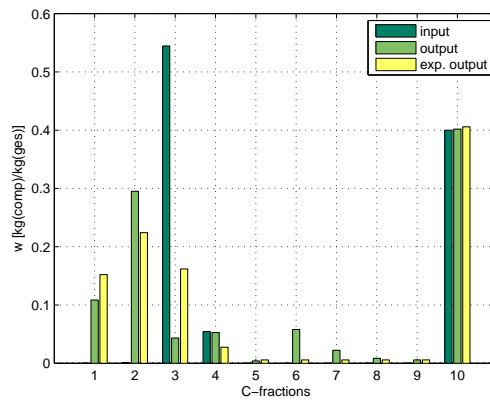


Figure 4.2: Feed and outflow composition and experimental results

The deviations from one result from numerical calculations, they are negligible. Figure 4.2 shows that the  $C_3$ -fractions are cracked to components with shorter chain lengths. One can see the steam ratio on the 10th bar, which represents all components without C-atoms. The experimental results are comparable with our

simulations. The deviations result from heuristical values, which we used for some chemical substances, and from numerical calculations.

## 4.2 Processes in the tube

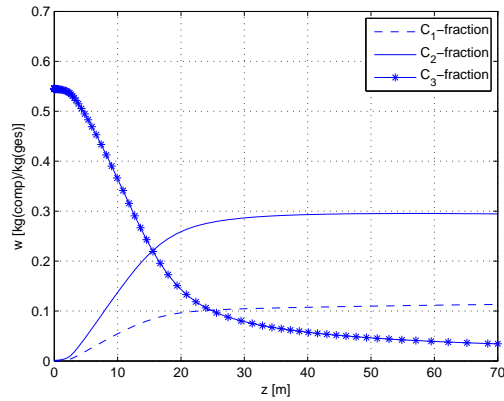


Figure 4.3: Different C-fractions over the tube length

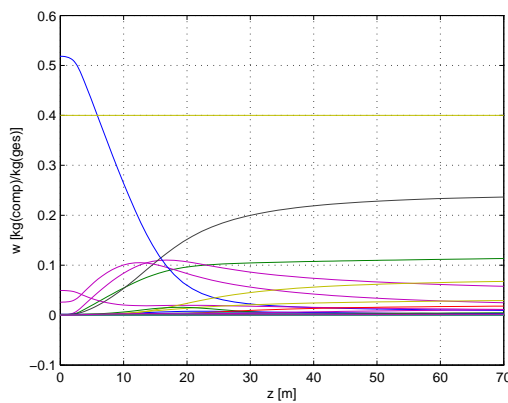


Figure 4.4: Not specified overview of the inner states(mass fractions)

In figure 4.3 one can see that long chains are cracked to shorter chains. Both the  $C_1$  and  $C_2$  fractions are produced. Moreover figure 4.4 shows that only few components change. The steam is not involved in the reaction scheme and keeps to a constant value.

### Mean chain length

$$\text{mean chain length}(z) = \beta_1^T \cdot \mathbf{w}(z) \quad (4.1)$$

In figure 4.5 is shown that the chain length decreases at the beginning. Caused by ethane formation the chain length increases until reaching the end of the tube.

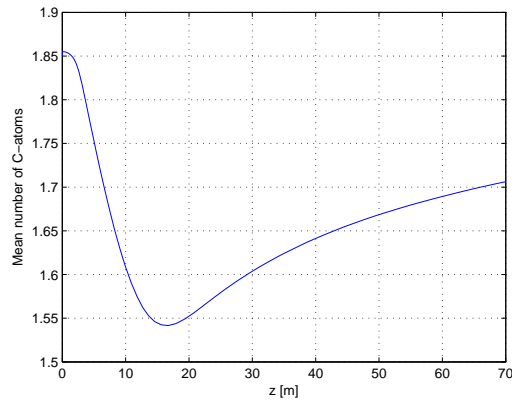


Figure 4.5: The mean chain length over the tube length

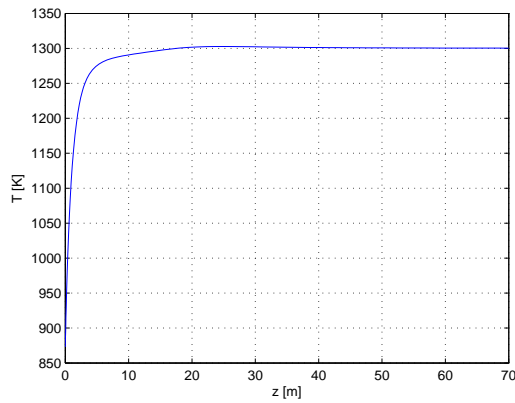


Figure 4.6: The temperature over the tube length

The progress of the inner temperature in figure 4.6 shows the following effects:

1. first section: no reaction and heating up to 1275 K
2. second section: the endotherm reactions start and heating is less effective
3. third section: the wall temperature can be achieved after 20 meters

### 4.3 Parameter studies and scale up

In order to find the best operating conditions of a steamcracker we modified the temperature of the wall (heating temperature), the retention time and steam ratio (l.a. figure 4.7 to 4.9). In this sequence we tried to find step by step the best parameter for a maximum yield of components with two C-atoms. We found that the following conditions are optimal:

$$T_{\text{wall}} = 1300 \text{ K} \quad (4.2)$$

$$\tau = 0.3 \text{ s} \quad (4.3)$$

$$x_{\text{steam}} = 0.4 \text{ wt\%} \quad (4.4)$$

This values are close to conditions which are used in industrial practice.

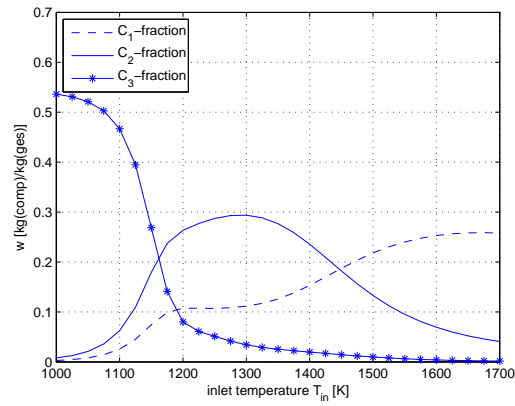


Figure 4.7: Variation of wall temperature

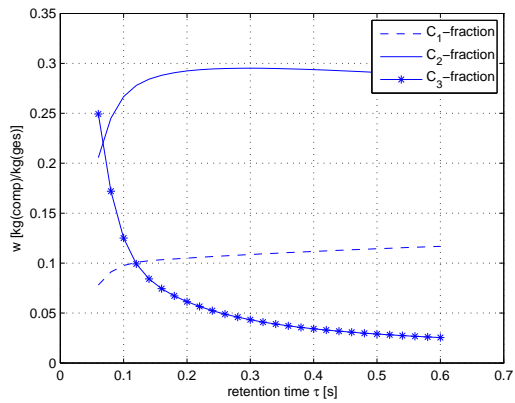


Figure 4.8: Variation of retention time

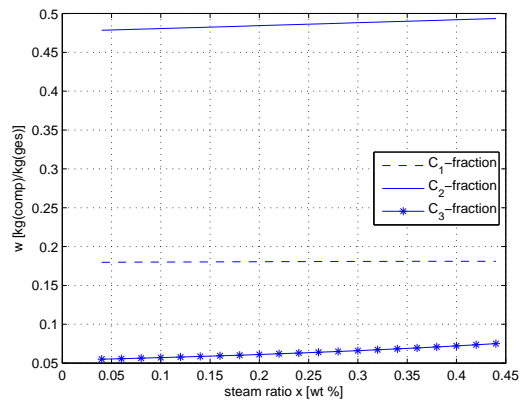


Figure 4.9: Variation of steam ratio

**Scale up** The results are given as mass fractions. If we want to scale up the steamcracker, we have to multiply the mass fractions with the feed stream(mass). The results of a steamcracker producing  $300000 \frac{t C_2 H_4}{a}$  are shown in table 4.1.

Table 4.1: Component mass flow

no.	$w [1]$	$\dot{m}_{in} [\frac{t}{a}]$	$w [1]$	$\dot{m}_{out} [\frac{t}{a}]$
1	0	0	0.0000	10
2	0	0	0.1102	508310
3	0	0	0.0004	1660
4	0	0	0.0000	0
5	0	0	0.0651	300000
6	0	0	0.0000	90
7	0.0009	4150	0.2298	1059670
8	0	0	0.0001	270
9	0	0	0.0001	250
10	0	0	0.0000	170
11	0	0	0.0000	0
12	0.0260	120070	0.0323	148850
13	0	0	0.0000	10
14	0	0	0.0000	10
15	0.5186	2391260	0.0117	54000
16	0	0	0.0016	7280
17	0	0	0.0000	20
18	0	0	0.0000	10
19	0	0	0.0000	0
20	0.0017	7840	0.0000	0
21	0.0017	7840	0.0040	18250
22	0.0017	7840	0.0032	14900
23	0	0	0.0000	10
24	0	0	0.0000	10
25	0	0	0.0000	0
26	0.0494	227700	0.0134	61910
27	0	0	0.0269	123950
28	0	0	0.0001	560
29	0	0	0.0034	15870
30	0	0	0.0000	0
31	0	0	0.0000	0
32	0	0	0.0000	0
33	0	0	0.0000	0
34	0	0	0.0628	289670
35	0	0	0.0000	0
36	0	0	0.0000	0
37	0	0	0.0007	3160
38	0	0	0.0161	74210
39	0	0	0.0021	9890
40	0	0	0.0087	40240
41	0	0	0.0001	330
42	0	0	0.0000	90
43	0	0	0.0017	7850
44	0	0	0.0032	14560
45	0	0	0.0004	1990
46	0	0	0.0000	0
47	0	0	0.0019	8620
48	0.4000	1844460	0.4000	1844460

## Chapter 5

### Conclusion

The optimised parameters resulting in 4.3 are close to the ones used in industrial steamcracking. The computed optimal temperature is about 1300 K and the industry uses temperatures between 1073 and 1173 K. The residence time of 0.3 seconds is in the preferred range of 0.2 to 0.5 seconds. For decreasing the partial pressure it is necessary to mix the naphtha with steam. Industry uses 0.5 wt% and we obtained 0.4 wt% as an optimal result for steam mass fraction.

While implementing the reaction scheme in MATLAB®, the mass balances has to be complied in every time step. This was proved by a self defined checkfunction. To achieve maximum computation speed in MATLAB®, we convert all equations in vectors to use the advantages of MATLAB®. Because of the module based structure of the code it is easily possible to upgrade our application e.g. by adding a bigger reaction network or changing parameters.

There are several approaches to extend our work. By implementing the pressure drop we could achieve more exact model equations. If one finds sources with bigger reaction networks and better material values our model will provide more precise results. The naphtha feed composition we got from several firms (Total and Shell) did not fit for our cause. A next step in simulation developing could be computation of the cracker start up behavior by discretizing the partial differential equations e.g. by finite volume method.

## Appendix A

### Reaction scheme<sup>1</sup>

#### A.1 Chain-initiation reactions

			$\log_{10} k_{\infty}$ <sup>2</sup>	$E_A$ [ $\frac{\text{kcal}}{\text{mol}}$ ]
1	$\text{C}_2\text{H}_6$	$\rightarrow 2\text{CH}_3\cdot$	17.04	89.0
2	$\text{C}_3\text{H}_8$	$\rightarrow \text{CH}_3\cdot + \text{C}_2\text{H}_5\cdot$	16.85	86.0
3	$1 - \text{C}_4\text{H}_8$	$\rightarrow \text{CH}_3\cdot + a - \text{C}_3\text{H}_5\cdot$	15.78	4.0
4	$\text{CyC}_5\text{H}_6$	$\rightarrow \text{H}\cdot + \text{CyC}_5\text{H}_5\cdot$	15.40	73.5
5	$\text{C}_6\text{H}_{10}$	$\rightarrow \text{CH}_3\cdot + \text{H}\cdot + \text{CyC}_5\text{H}_6$	16.20	72.0
6	Diallyl	$\rightarrow 2a - \text{C}_3\text{H}_5\cdot$	14.78	59.0
7	$\text{Me} - \text{CyC}_5\text{H}_7$	$\rightarrow \text{CH}_3\cdot + \text{H}\cdot + \text{CyC}_5\text{H}_6$	16.00	72.0
8	$\text{Me} - \text{CyC}_5\text{H}_5$	$\rightarrow 2\text{H}\cdot + \text{C}_6\text{H}_6$	15.48	73.5
9	$\text{C}_2\text{H}_4 + \text{CyC}_5\text{H}_6$	$\rightarrow \text{H}\cdot + \text{CH}_3\cdot + \text{C}_6\text{H}_6$	8.70	30.0
10	$\text{C}_3\text{H}_6 + \text{CyC}_5\text{H}_6$	$\rightarrow 2\text{CH}_3\cdot + \text{C}_6\text{H}_6$	8.70	30.0
11	$n - \text{C}_4\text{H}_{10}$	$\rightarrow 2\text{C}_2\text{H}_5\cdot$	16.70	83.0

#### A.2 H Abstraction reactions

			$\log_{10} k_{\infty}$	$E_A$ [ $\frac{\text{kcal}}{\text{mol}}$ ]
12	$\text{H}\cdot + \text{H}_2$	$\rightarrow \text{H}_2 + \text{H}\cdot$	11.06	8.0
13	$\text{H}\cdot + \text{CH}_4$	$\rightarrow \text{H}_2 + \text{CH}_3\cdot$	11.06	8.0
14	$\text{H}\cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{H}_2 + \text{C}_2\text{H}_3\cdot$	11.06	8.0
15	$\text{H}\cdot + \text{C}_2\text{H}_6$	$\rightarrow \text{H}_2 + \text{C}_2\text{H}_5\cdot$	11.06	8.0
16	$\text{H}\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{H}_2 + a - \text{C}_3\text{H}_5\cdot$	11.06	8.0
17	$\text{H}\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{H}_2 + v - \text{C}_3\text{H}_5\cdot$	11.06	8.0
18	$\text{H}\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{H}_2 + 1 - \text{C}_3\text{H}_7\cdot$	11.06	8.0
19	$\text{H}\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{H}_2 + 2 - \text{C}_3\text{H}_7\cdot$	11.06	8.0
20	$\text{H}\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{H}_2 + a - \text{C}_4\text{H}_7\cdot$	11.06	8.0
21	$\text{H}\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{H}_2 + 4 - \text{C}_4\text{H}_7\cdot$	11.06	8.0
22	$\text{H}\cdot + 2 - \text{C}_4\text{H}_8$	$\rightarrow \text{H}_2 + a - \text{C}_4\text{H}_7\cdot$	11.06	8.0
23	$\text{H}\cdot + \text{iso} - \text{C}_4\text{H}_8$	$\rightarrow \text{H}_2 + \text{iso} - \text{C}_4\text{H}_7\cdot$	11.06	8.0
24	$\text{H}\cdot + \text{C}_5\text{H}_8$	$\rightarrow \text{H}_2 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	11.06	8.0
25	$\text{H}\cdot + \text{CyC}_5\text{H}_8$	$\rightarrow \text{H}_2 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	11.06	8.0
26	$\text{H}\cdot + \text{CyC}_5\text{H}_6$	$\rightarrow \text{H}_2 + \text{CyC}_5\text{H}_5\cdot$	11.06	8.0
27	$\text{H}\cdot + \text{C}_6\text{H}_{10}$	$\rightarrow \text{H}_2 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	11.06	8.0
28	$\text{H}\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{H}_2 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	11.06	8.0
29	$\text{H}\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{H}_2 + \text{H}\cdot + \text{MeCyC}_5\text{H}_5$	11.06	8.0
30	$\text{H}\cdot + \text{MeCyC}_5\text{H}_5$	$\rightarrow \text{H}_2 + \text{H}\cdot + \text{C}_6\text{H}_6$	11.06	8.0

<sup>1</sup>Reaction scheme taken from [DR83]

<sup>2</sup>For unimolecular reactions  $[k_{\infty}] = \frac{1}{s}$ ; for bimolecular reactions  $[k_{\infty}] = \frac{l}{\text{mol}\cdot\text{s}}$

31	$\text{H}\cdot + \text{C}_7\text{H}_8$	$\rightarrow \text{H}_2 + \text{C}_7\text{H}_7\cdot$	11.06	8.0
32	$\text{H}\cdot + \text{C}_8\text{H}_{10}$	$\rightarrow \text{H}_2 + \text{C}_8\text{H}_9\cdot$	11.06	8.0
33	$\text{H}\cdot + \text{n} - \text{C}_4\text{H}_{10}$	$\rightarrow \text{H}_2 + 1 - \text{C}_4\text{H}_9\cdot$	11.06	8.0
34	$\text{H}\cdot + \text{n} - \text{C}_4\text{H}_{10}$	$\rightarrow \text{H}_2 + 2 - \text{C}_4\text{H}_9\cdot$	11.06	8.0
35	$\text{H}\cdot + \text{CyC}_6\text{H}_{10}$	$\rightarrow \text{H}_2 + \text{H}\cdot + \text{H}_2 + \text{C}_6\text{H}_6$	11.06	8.0
36	$\text{CH}_3\cdot + \text{H}_2$	$\rightarrow \text{CH}_4 + \text{H}\cdot$	9.18	11.9
37	$\text{CH}_3\cdot + \text{CH}_4$	$\rightarrow \text{CH}_4 + \text{CH}_3\cdot$	9.18	11.9
38	$\text{CH}_3\cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{CH}_4 + \text{C}_2\text{H}_3\cdot$	9.18	11.9
39	$\text{CH}_3\cdot + \text{C}_2\text{H}_6$	$\rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\cdot$	9.18	11.9
40	$\text{CH}_3\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{CH}_4 + \text{a} - \text{C}_3\text{H}_5\cdot$	9.18	11.9
41	$\text{CH}_3\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{CH}_4 + \text{v} - \text{C}_3\text{H}_5\cdot$	9.18	11.9
42	$\text{CH}_3\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{CH}_4 + 1 - \text{C}_3\text{H}_7\cdot$	9.18	11.9
43	$\text{CH}_3\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{CH}_4 + 2 - \text{C}_3\text{H}_7\cdot$	9.18	11.9
44	$\text{CH}_3\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{CH}_4 + \text{a} - \text{C}_4\text{H}_7\cdot$	9.18	11.9
45	$\text{CH}_3\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{CH}_4 + 4 - \text{C}_4\text{H}_7\cdot$	9.18	11.9
46	$\text{CH}_3\cdot + 2 - \text{C}_4\text{H}_8$	$\rightarrow \text{CH}_4 + \text{a} - \text{C}_4\text{H}_7\cdot$	9.18	11.9
47	$\text{CH}_3\cdot + \text{iso} - \text{C}_4\text{H}_8$	$\rightarrow \text{CH}_4 + \text{iso} - \text{C}_4\text{H}_7\cdot$	9.18	11.9
48	$\text{CH}_3\cdot + \text{C}_5\text{H}_8$	$\rightarrow \text{CH}_4 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	9.18	11.9
49	$\text{CH}_3\cdot + \text{CyC}_5\text{H}_8$	$\rightarrow \text{CH}_4 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	9.18	11.9
50	$\text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	$\rightarrow \text{CH}_4 + \text{CyC}_5\text{H}_5\cdot$	9.18	11.9
51	$\text{CH}_3\cdot + \text{C}_6\text{H}_{10}$	$\rightarrow \text{CH}_4 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	9.18	11.9
52	$\text{CH}_3\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{CH}_4 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	9.18	11.9
53	$\text{CH}_3\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{CH}_4 + \text{H}\cdot + \text{MeCyC}_5\text{H}_5$	9.18	11.9
54	$\text{CH}_3\cdot + \text{MeCyC}_5\text{H}_5$	$\rightarrow \text{CH}_4 + \text{H}\cdot + \text{C}_6\text{H}_6$	9.18	11.9
55	$\text{CH}_3\cdot + \text{C}_7\text{H}_8$	$\rightarrow \text{CH}_4 + \text{C}_7\text{H}_7\cdot$	9.18	11.9
56	$\text{CH}_3\cdot + \text{C}_8\text{H}_{10}$	$\rightarrow \text{CH}_4 + \text{C}_8\text{H}_9\cdot$	9.18	11.9
57	$\text{CH}_3\cdot + \text{n} - \text{C}_4\text{H}_{10}$	$\rightarrow \text{CH}_4 + 1 - \text{C}_4\text{H}_9\cdot$	9.18	11.9
58	$\text{CH}_3\cdot + \text{n} - \text{C}_4\text{H}_{10}$	$\rightarrow \text{CH}_4 + 2 - \text{C}_4\text{H}_9\cdot$	9.18	11.9
59	$\text{CH}_3\cdot + \text{CyC}_6\text{H}_{10}$	$\rightarrow \text{CH}_4 + \text{H}\cdot + \text{H}_2 + \text{C}_6\text{H}_6$	9.18	11.9
60	$\text{C}_2\text{H}_3\cdot + \text{H}_2$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot$	9.10	7.8
61	$\text{C}_2\text{H}_3\cdot + \text{CH}_4$	$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot$	9.10	7.8
62	$\text{C}_2\text{H}_3\cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3\cdot$	9.10	7.8
63	$\text{C}_2\text{H}_3\cdot + \text{C}_2\text{H}_6$	$\rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\cdot$	9.10	7.8
64	$\text{C}_2\text{H}_3\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{C}_2\text{H}_4 + \text{a} - \text{C}_3\text{H}_5\cdot$	9.10	7.8
65	$\text{C}_2\text{H}_3\cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{C}_2\text{H}_4 + \text{v} - \text{C}_3\text{H}_5\cdot$	9.10	7.8
66	$\text{C}_2\text{H}_3\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + 1 - \text{C}_3\text{H}_7\cdot$	9.10	7.8
67	$\text{C}_2\text{H}_3\cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + 2 - \text{C}_3\text{H}_7\cdot$	9.10	7.8
68	$\text{C}_2\text{H}_3\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{a} - \text{C}_4\text{H}_7\cdot$	9.10	7.8
69	$\text{C}_2\text{H}_3\cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + 4 - \text{C}_4\text{H}_7\cdot$	9.10	7.8
70	$\text{C}_2\text{H}_3\cdot + 2 - \text{C}_4\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{a} - \text{C}_4\text{H}_7\cdot$	9.10	7.8
71	$\text{C}_2\text{H}_3\cdot + \text{iso} - \text{C}_4\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{iso} - \text{C}_4\text{H}_7\cdot$	9.10	7.8
72	$\text{C}_2\text{H}_3\cdot + \text{C}_5\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	9.10	7.8
73	$\text{C}_2\text{H}_3\cdot + \text{CyC}_5\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot + \text{CyC}_5\text{H}_6$	9.10	7.8
74	$\text{C}_2\text{H}_3\cdot + \text{CyC}_5\text{H}_6$	$\rightarrow \text{C}_2\text{H}_4 + \text{CyC}_5\text{H}_5\cdot$	9.10	7.8
75	$\text{C}_2\text{H}_3\cdot + \text{C}_6\text{H}_{10}$	$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	9.10	7.8
76	$\text{C}_2\text{H}_3\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot + \text{CyC}_5\text{H}_6$	9.10	7.8
77	$\text{C}_2\text{H}_3\cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot + \text{MeCyC}_5\text{H}_5$	9.10	7.8
78	$\text{C}_2\text{H}_3\cdot + \text{MeCyC}_5\text{H}_5$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot + \text{C}_6\text{H}_6$	9.10	7.8
79	$\text{C}_2\text{H}_3\cdot + \text{C}_7\text{H}_8$	$\rightarrow \text{C}_2\text{H}_4 + \text{C}_7\text{H}_7\cdot$	9.10	7.8
80	$\text{C}_2\text{H}_3\cdot + \text{C}_8\text{H}_{10}$	$\rightarrow \text{C}_2\text{H}_4 + \text{C}_8\text{H}_9\cdot$	9.10	7.8

81	$C_2H_3 \cdot + n - C_4H_{10}$	$\rightarrow C_2H_4 + 1 - C_4H_9 \cdot$	9.10	7.8
82	$C_2H_3 \cdot + n - C_4H_{10}$	$\rightarrow C_2H_4 + 2 - C_4H_9 \cdot$	9.10	7.8
83	$C_2H_3 \cdot + CyC_6H_{10}$	$\rightarrow C_2H_4 + H \cdot + H_2 + C_6H_6$	9.10	7.8
84	$C_2H_5 \cdot + H_2$	$\rightarrow C_2H_6 + H \cdot$	9.08	14.0
85	$C_2H_5 \cdot + CH_4$	$\rightarrow C_2H_6 + CH_3 \cdot$	9.08	14.0
86	$C_2H_5 \cdot + C_2H_4$	$\rightarrow C_2H_6 + C_2H_3 \cdot$	9.08	14.0
87	$C_2H_5 \cdot + C_2H_6$	$\rightarrow C_2H_6 + C_2H_5 \cdot$	9.08	14.0
88	$C_2H_5 \cdot + C_3H_6$	$\rightarrow C_2H_6 + a - C_3H_5 \cdot$	9.08	14.0
89	$C_2H_5 \cdot + C_3H_6$	$\rightarrow C_2H_6 + v - C_3H_5 \cdot$	9.08	14.0
90	$C_2H_5 \cdot + C_3H_8$	$\rightarrow C_2H_6 + 1 - C_3H_7 \cdot$	9.08	14.0
91	$C_2H_5 \cdot + C_3H_8$	$\rightarrow C_2H_6 + 2 - C_3H_7 \cdot$	9.08	14.0
92	$C_2H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_2H_6 + a - C_4H_7 \cdot$	9.08	14.0
93	$C_2H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_2H_6 + 4 - C_4H_7 \cdot$	9.08	14.0
94	$C_2H_5 \cdot + 2 - C_4H_8$	$\rightarrow C_2H_6 + a - C_4H_7 \cdot$	9.08	14.0
95	$C_2H_5 \cdot + iso - C_4H_8$	$\rightarrow C_2H_6 + iso - C_4H_7 \cdot$	9.08	14.0
96	$C_2H_5 \cdot + C_5H_8$	$\rightarrow C_2H_6 + H \cdot + CyC_5H_6$	9.08	14.0
97	$C_2H_5 \cdot + CyC_5H_8$	$\rightarrow C_2H_6 + H \cdot + CyC_5H_6$	9.08	14.0
98	$C_2H_5 \cdot + CyC_5H_6$	$\rightarrow C_2H_6 + CyC_5H_5 \cdot$	9.08	14.0
99	$C_2H_5 \cdot + C_6H_{10}$	$\rightarrow C_2H_6 + CH_3 \cdot + CyC_5H_6$	9.08	14.0
100	$C_2H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_2H_6 + CH_3 \cdot + CyC_5H_6$	9.08	14.0
101	$C_2H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_2H_6 + H \cdot + MeCyC_5H_5$	9.08	14.0
102	$C_2H_5 \cdot + MeCyC_5H_5$	$\rightarrow C_2H_6 + H \cdot + C_6H_6$	9.08	14.0
103	$C_2H_5 \cdot + C_7H_8$	$\rightarrow C_2H_6 + C_7H_7 \cdot$	9.08	14.0
104	$C_2H_5 \cdot + C_8H_{10}$	$\rightarrow C_2H_6 + C_8H_9 \cdot$	9.08	14.0
105	$C_2H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_2H_6 + 1 - C_4H_9 \cdot$	9.08	14.0
106	$C_2H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_2H_6 + 2 - C_4H_9 \cdot$	9.08	14.0
107	$C_2H_5 \cdot + CyC_6H_{10}$	$\rightarrow C_2H_6 + H \cdot + H_2 + C_6H_6$	9.08	14.0
108	$a - C_3H_5 \cdot + H_2$	$\rightarrow C_3H_6 + H \cdot$	9.60	23.5
109	$a - C_3H_5 \cdot + CH_4$	$\rightarrow C_3H_6 + CH_3 \cdot$	9.60	23.5
110	$a - C_3H_5 \cdot + C_2H_4$	$\rightarrow C_3H_6 + C_2H_3 \cdot$	9.60	23.5
111	$a - C_3H_5 \cdot + C_2H_6$	$\rightarrow C_3H_6 + C_2H_5 \cdot$	9.60	23.5
112	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_3H_6 + a - C_3H_5 \cdot$	9.60	23.5
113	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_3H_6 + v - C_3H_5 \cdot$	9.60	23.5
114	$a - C_3H_5 \cdot + C_3H_8$	$\rightarrow C_3H_6 + 1 - C_3H_7 \cdot$	9.60	23.5
115	$a - C_3H_5 \cdot + C_3H_8$	$\rightarrow C_3H_6 + 2 - C_3H_7 \cdot$	9.60	23.5
116	$a - C_3H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_6 + a - C_4H_7 \cdot$	9.60	23.5
117	$a - C_3H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_6 + 4 - C_4H_7 \cdot$	9.60	23.5
118	$a - C_3H_5 \cdot + 2 - C_4H_8$	$\rightarrow C_3H_6 + a - C_4H_7 \cdot$	9.60	23.5
119	$a - C_3H_5 \cdot + iso - C_4H_8$	$\rightarrow C_3H_6 + iso - C_4H_7 \cdot$	9.60	23.5
120	$a - C_3H_5 \cdot + C_5H_8$	$\rightarrow C_3H_6 + H \cdot + CyC_5H_6$	9.60	23.5
121	$a - C_3H_5 \cdot + CyC_5H_8$	$\rightarrow C_3H_6 + H \cdot + CyC_5H_6$	9.60	23.5
122	$a - C_3H_5 \cdot + CyC_5H_6$	$\rightarrow C_3H_6 + CyC_5H_5 \cdot$	9.60	23.5
123	$a - C_3H_5 \cdot + C_6H_{10}$	$\rightarrow C_3H_6 + CH_3 \cdot + CyC_5H_6$	9.60	23.5
124	$a - C_3H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_6 + CH_3 \cdot + CyC_5H_6$	9.60	23.5
125	$a - C_3H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_6 + H \cdot + MeCyC_5H_5$	9.60	23.5
126	$a - C_3H_5 \cdot + MeCyC_5H_5$	$\rightarrow C_3H_6 + H \cdot + C_6H_6$	9.60	23.5
127	$a - C_3H_5 \cdot + C_7H_8$	$\rightarrow C_3H_6 + C_7H_7 \cdot$	9.60	23.5
128	$a - C_3H_5 \cdot + C_8H_{10}$	$\rightarrow C_3H_6 + C_8H_9 \cdot$	9.60	23.5
129	$a - C_3H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_6 + 1 - C_4H_9 \cdot$	9.60	23.5
130	$a - C_3H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_6 + 2 - C_4H_9 \cdot$	9.60	23.5

131	$a - C_3H_5 \cdot + CyC_6H_{10}$	$\rightarrow C_3H_6 + H \cdot + H_2 + C_6H_6$	9.60	23.5
132	$v - C_3H_5 \cdot + H_2$	$\rightarrow C_3H_6 + H \cdot$	9.10	7.8
133	$v - C_3H_5 \cdot + CH_4$	$\rightarrow C_3H_6 + CH_3 \cdot$	9.10	7.8
134	$v - C_3H_5 \cdot + C_2H_4$	$\rightarrow C_3H_6 + C_2H_3 \cdot$	9.10	7.8
135	$v - C_3H_5 \cdot + C_2H_6$	$\rightarrow C_3H_6 + C_2H_5 \cdot$	9.10	7.8
136	$v - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_3H_6 + a - C_3H_5 \cdot$	9.10	7.8
137	$v - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_3H_6 + v - C_3H_5 \cdot$	9.10	7.8
138	$v - C_3H_5 \cdot + C_3H_8$	$\rightarrow C_3H_6 + 1 - C_3H_7 \cdot$	9.10	7.8
139	$v - C_3H_5 \cdot + C_3H_8$	$\rightarrow C_3H_6 + 2 - C_3H_7 \cdot$	9.10	7.8
140	$v - C_3H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_6 + a - C_4H_7 \cdot$	9.10	7.8
141	$v - C_3H_5 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_6 + 4 - C_4H_7 \cdot$	9.10	7.8
142	$v - C_3H_5 \cdot + 2 - C_4H_8$	$\rightarrow C_3H_6 + a - C_4H_7 \cdot$	9.10	7.8
143	$v - C_3H_5 \cdot + iso - C_4H_8$	$\rightarrow C_3H_6 + iso - C_4H_7 \cdot$	9.10	7.8
144	$v - C_3H_5 \cdot + C_5H_8$	$\rightarrow C_3H_6 + H \cdot + CyC_5H_6$	9.10	7.8
145	$v - C_3H_5 \cdot + CyC_5H_8$	$\rightarrow C_3H_6 + H \cdot + CyC_5H_6$	9.10	7.8
146	$v - C_3H_5 \cdot + CyC_5H_6$	$\rightarrow C_3H_6 + CyC_5H_5 \cdot$	9.10	7.8
147	$v - C_3H_5 \cdot + C_6H_{10}$	$\rightarrow C_3H_6 + CH_3 \cdot + CyC_5H_6$	9.10	7.8
148	$v - C_3H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_6 + CH_3 \cdot + CyC_5H_6$	9.10	7.8
149	$v - C_3H_5 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_6 + H \cdot + MeCyC_5H_5$	9.10	7.8
150	$v - C_3H_5 \cdot + MeCyC_5H_5$	$\rightarrow C_3H_6 + H \cdot + C_6H_6$	9.10	7.8
151	$v - C_3H_5 \cdot + C_7H_8$	$\rightarrow C_3H_6 + C_7H_7 \cdot$	9.10	7.8
152	$v - C_3H_5 \cdot + C_8H_{10}$	$\rightarrow C_3H_6 + C_8H_9 \cdot$	9.10	7.8
153	$v - C_3H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_6 + 1 - C_4H_9 \cdot$	9.10	7.8
154	$v - C_3H_5 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_6 + 2 - C_4H_9 \cdot$	9.10	7.8
155	$v - C_3H_5 \cdot + CyC_6H_{10}$	$\rightarrow C_3H_6 + H \cdot + H_2 + C_6H_6$	9.10	7.8
156	$2 - C_3H_7 \cdot + H_2$	$\rightarrow C_3H_8 + H \cdot$	8.90	15.5
157	$2 - C_3H_7 \cdot + CH_4$	$\rightarrow C_3H_8 + CH_3 \cdot$	8.90	15.5
158	$2 - C_3H_7 \cdot + C_2H_4$	$\rightarrow C_3H_8 + C_2H_3 \cdot$	8.90	15.5
159	$2 - C_3H_7 \cdot + C_2H_6$	$\rightarrow C_3H_8 + C_2H_5 \cdot$	8.90	15.5
160	$2 - C_3H_7 \cdot + C_3H_6$	$\rightarrow C_3H_8 + a - C_3H_5 \cdot$	8.90	15.5
161	$2 - C_3H_7 \cdot + C_3H_6$	$\rightarrow C_3H_8 + v - C_3H_5 \cdot$	8.90	15.5
162	$2 - C_3H_7 \cdot + C_3H_8$	$\rightarrow C_3H_8 + 1 - C_3H_7 \cdot$	8.90	15.5
163	$2 - C_3H_7 \cdot + C_3H_8$	$\rightarrow C_3H_8 + 2 - C_3H_7 \cdot$	8.90	15.5
164	$2 - C_3H_7 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_8 + a - C_4H_7 \cdot$	8.90	15.5
165	$2 - C_3H_7 \cdot + 1 - C_4H_8$	$\rightarrow C_3H_8 + 4 - C_4H_7 \cdot$	8.90	15.5
166	$2 - C_3H_7 \cdot + 2 - C_4H_8$	$\rightarrow C_3H_8 + a - C_4H_7 \cdot$	8.90	15.5
167	$2 - C_3H_7 \cdot + iso - C_4H_8$	$\rightarrow C_3H_8 + iso - C_4H_7 \cdot$	8.90	15.5
168	$2 - C_3H_7 \cdot + C_5H_8$	$\rightarrow C_3H_8 + H \cdot + CyC_5H_6$	8.90	15.5
169	$2 - C_3H_7 \cdot + CyC_5H_8$	$\rightarrow C_3H_8 + H \cdot + CyC_5H_6$	8.90	15.5
170	$2 - C_3H_7 \cdot + CyC_5H_6$	$\rightarrow C_3H_8 + CyC_5H_5 \cdot$	8.90	15.5
171	$2 - C_3H_7 \cdot + C_6H_{10}$	$\rightarrow C_3H_8 + CH_3 \cdot + CyC_5H_6$	8.90	15.5
172	$2 - C_3H_7 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_8 + CH_3 \cdot + CyC_5H_6$	8.90	15.5
173	$2 - C_3H_7 \cdot + MeCyC_5H_7$	$\rightarrow C_3H_8 + H \cdot + MeCyC_5H_5$	8.90	15.5
174	$2 - C_3H_7 \cdot + MeCyC_5H_5$	$\rightarrow C_3H_8 + H \cdot + C_6H_6$	8.90	15.5
175	$2 - C_3H_7 \cdot + C_7H_8$	$\rightarrow C_3H_8 + C_7H_7 \cdot$	8.90	15.5
176	$2 - C_3H_7 \cdot + C_8H_{10}$	$\rightarrow C_3H_8 + C_8H_9 \cdot$	8.90	15.5
177	$2 - C_3H_7 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_8 + 1 - C_4H_9 \cdot$	8.90	15.5
178	$2 - C_3H_7 \cdot + n - C_4H_{10}$	$\rightarrow C_3H_8 + 2 - C_4H_9 \cdot$	8.90	15.5
179	$2 - C_3H_7 \cdot + CyC_6H_{10}$	$\rightarrow C_3H_8 + H \cdot + H_2 + C_6H_6$	8.90	15.5
180	$2 - C_4H_9 \cdot + H_2$	$\rightarrow C_4H_{10} + H \cdot$	8.90	15.5

181	$2 - C_4H_9 \cdot + CH_4$	$\rightarrow C_4H_{10} + CH_3 \cdot$	8.90	15.5
182	$2 - C_4H_9 \cdot + C_2H_4$	$\rightarrow C_4H_{10} + C_2H_3 \cdot$	8.90	15.5
183	$2 - C_4H_9 \cdot + C_2H_6$	$\rightarrow C_4H_{10} + C_2H_5 \cdot$	8.90	15.5
184	$2 - C_4H_9 \cdot + C_3H_6$	$\rightarrow C_4H_{10} + a - C_3H_5 \cdot$	8.90	15.5
185	$2 - C_4H_9 \cdot + C_3H_6$	$\rightarrow C_4H_{10} + v - C_3H_5 \cdot$	8.90	15.5
186	$2 - C_4H_9 \cdot + C_3H_8$	$\rightarrow C_4H_{10} + 1 - C_3H_7 \cdot$	8.90	15.5
187	$2 - C_4H_9 \cdot + C_3H_8$	$\rightarrow C_4H_{10} + 2 - C_3H_7 \cdot$	8.90	15.5
188	$2 - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow C_4H_{10} + a - C_4H_7 \cdot$	8.90	15.5
189	$2 - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow C_4H_{10} + 4 - C_4H_7 \cdot$	8.90	15.5
190	$2 - C_4H_9 \cdot + 2 - C_4H_8$	$\rightarrow C_4H_{10} + a - C_4H_7 \cdot$	8.90	15.5
191	$2 - C_4H_9 \cdot + iso - C_4H_8$	$\rightarrow C_4H_{10} + iso - C_4H_7 \cdot$	8.90	15.5
192	$2 - C_4H_9 \cdot + C_5H_8$	$\rightarrow C_4H_{10} + H \cdot + CyC_5H_6$	8.90	15.5
193	$2 - C_4H_9 \cdot + CyC_5H_8$	$\rightarrow C_4H_{10} + H \cdot + CyC_5H_6$	8.90	15.5
194	$2 - C_4H_9 \cdot + CyC_5H_6$	$\rightarrow C_4H_{10} + CyC_5H_5 \cdot$	8.90	15.5
195	$2 - C_4H_9 \cdot + C_6H_{10}$	$\rightarrow C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	15.5
196	$2 - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	15.5
197	$2 - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow C_4H_{10} + H \cdot + MeCyC_5H_5$	8.90	15.5
198	$2 - C_4H_9 \cdot + MeCyC_5H_5$	$\rightarrow C_4H_{10} + H \cdot + C_6H_6$	8.90	15.5
199	$2 - C_4H_9 \cdot + C_7H_8$	$\rightarrow C_4H_{10} + C_7H_7 \cdot$	8.90	15.5
200	$2 - C_4H_9 \cdot + C_8H_{10}$	$\rightarrow C_4H_{10} + C_8H_9 \cdot$	8.90	15.5
201	$2 - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow C_4H_{10} + 1 - C_4H_9 \cdot$	8.90	15.5
202	$2 - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow C_4H_{10} + 2 - C_4H_9 \cdot$	8.90	15.5
203	$2 - C_4H_9 \cdot + CyC_6H_{10}$	$\rightarrow C_4H_{10} + H \cdot + H_2 + C_6H_6$	8.90	15.5
204	$a - C_4H_7 \cdot + H_2$	$\rightarrow 2 - C_4H_8 + H \cdot$	9.60	24.0
205	$a - C_4H_7 \cdot + CH_4$	$\rightarrow 2 - C_4H_8 + CH_3 \cdot$	9.60	24.0
206	$a - C_4H_7 \cdot + C_2H_4$	$\rightarrow 2 - C_4H_8 + C_2H_3 \cdot$	9.60	24.0
207	$a - C_4H_7 \cdot + C_2H_6$	$\rightarrow 2 - C_4H_8 + C_2H_5 \cdot$	9.60	24.0
208	$a - C_4H_7 \cdot + C_3H_6$	$\rightarrow 2 - C_4H_8 + a - C_3H_5 \cdot$	9.60	24.0
209	$a - C_4H_7 \cdot + C_3H_6$	$\rightarrow 2 - C_4H_8 + v - C_3H_5 \cdot$	9.60	24.0
210	$a - C_4H_7 \cdot + C_3H_8$	$\rightarrow 2 - C_4H_8 + 1 - C_3H_7 \cdot$	9.60	24.0
211	$a - C_4H_7 \cdot + C_3H_8$	$\rightarrow 2 - C_4H_8 + 2 - C_3H_7 \cdot$	9.60	24.0
212	$a - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow 2 - C_4H_8 + a - C_4H_7 \cdot$	9.60	24.0
213	$a - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow 2 - C_4H_8 + 4 - C_4H_7 \cdot$	9.60	24.0
214	$a - C_4H_7 \cdot + 2 - C_4H_8$	$\rightarrow 2 - C_4H_8 + a - C_4H_7 \cdot$	9.60	24.0
215	$a - C_4H_7 \cdot + iso - C_4H_8$	$\rightarrow 2 - C_4H_8 + iso - C_4H_7 \cdot$	9.60	24.0
216	$a - C_4H_7 \cdot + C_5H_8$	$\rightarrow 2 - C_4H_8 + H \cdot + CyC_5H_6$	9.60	24.0
217	$a - C_4H_7 \cdot + CyC_5H_8$	$\rightarrow 2 - C_4H_8 + H \cdot + CyC_5H_6$	9.60	24.0
218	$a - C_4H_7 \cdot + CyC_5H_6$	$\rightarrow 2 - C_4H_8 + CyC_5H_5 \cdot$	9.60	24.0
219	$a - C_4H_7 \cdot + C_6H_{10}$	$\rightarrow 2 - C_4H_8 + CH_3 \cdot + CyC_5H_6$	9.60	24.0
220	$a - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow 2 - C_4H_8 + CH_3 \cdot + CyC_5H_6$	9.60	24.0
221	$a - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow 2 - C_4H_8 + H \cdot + MeCyC_5H_5$	9.60	24.0
222	$a - C_4H_7 \cdot + MeCyC_5H_5$	$\rightarrow 2 - C_4H_8 + H \cdot + C_6H_6$	9.60	24.0
223	$a - C_4H_7 \cdot + C_7H_8$	$\rightarrow 2 - C_4H_8 + C_7H_7 \cdot$	9.60	24.0
224	$a - C_4H_7 \cdot + C_8H_{10}$	$\rightarrow 2 - C_4H_8 + C_8H_9 \cdot$	9.60	24.0
225	$a - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow 2 - C_4H_8 + 1 - C_4H_9 \cdot$	9.60	24.0
226	$a - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow 2 - C_4H_8 + 2 - C_4H_9 \cdot$	9.60	24.0
227	$a - C_4H_7 \cdot + CyC_6H_{10}$	$\rightarrow 2 - C_4H_8 + H \cdot + H_2 + C_6H_6$	9.60	24.0
228	$4 - C_4H_7 \cdot + H_2$	$\rightarrow 1 - C_4H_8 + H \cdot$	8.9	12.2
229	$4 - C_4H_7 \cdot + CH_4$	$\rightarrow 1 - C_4H_8 + CH_3 \cdot$	8.9	12.2
230	$4 - C_4H_7 \cdot + C_2H_4$	$\rightarrow 1 - C_4H_8 + C_2H_3 \cdot$	8.9	12.2

231	$4 - C_4H_7 \cdot + C_2H_6$	$\rightarrow 1 - C_4H_8 + C_2H_5 \cdot$	8.9	12.2
232	$4 - C_4H_7 \cdot + C_3H_6$	$\rightarrow 1 - C_4H_8 + a - C_3H_5 \cdot$	8.9	12.2
233	$4 - C_4H_7 \cdot + C_3H_6$	$\rightarrow 1 - C_4H_8 + v - C_3H_5 \cdot$	8.9	12.2
234	$4 - C_4H_7 \cdot + C_3H_8$	$\rightarrow 1 - C_4H_8 + 1 - C_3H_7 \cdot$	8.9	12.2
235	$4 - C_4H_7 \cdot + C_3H_8$	$\rightarrow 1 - C_4H_8 + 2 - C_3H_7 \cdot$	8.9	12.2
236	$4 - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow 1 - C_4H_8 + a - C_4H_7 \cdot$	8.9	12.2
237	$4 - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow 1 - C_4H_8 + 4 - C_4H_7 \cdot$	8.9	12.2
238	$4 - C_4H_7 \cdot + 2 - C_4H_8$	$\rightarrow 1 - C_4H_8 + a - C_4H_7 \cdot$	8.9	12.2
239	$4 - C_4H_7 \cdot + iso - C_4H_8$	$\rightarrow 1 - C_4H_8 + iso - C_4H_7 \cdot$	8.9	12.2
240	$4 - C_4H_7 \cdot + C_5H_8$	$\rightarrow 1 - C_4H_8 + H \cdot + CyC_5H_6$	8.9	12.2
241	$4 - C_4H_7 \cdot + CyC_5H_8$	$\rightarrow 1 - C_4H_8 + H \cdot + CyC_5H_6$	8.9	12.2
242	$4 - C_4H_7 \cdot + CyC_5H_6$	$\rightarrow 1 - C_4H_8 + CyC_5H_5 \cdot$	8.9	12.2
243	$4 - C_4H_7 \cdot + C_6H_{10}$	$\rightarrow 1 - C_4H_8 + CH_3 \cdot + CyC_5H_6$	8.9	12.2
244	$4 - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow 1 - C_4H_8 + CH_3 \cdot + CyC_5H_6$	8.9	12.2
245	$4 - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow 1 - C_4H_8 + H \cdot + MeCyC_5H_5$	8.9	12.2
246	$4 - C_4H_7 \cdot + MeCyC_5H_5$	$\rightarrow 1 - C_4H_8 + H \cdot + C_6H_6$	8.9	12.2
247	$4 - C_4H_7 \cdot + C_7H_8$	$\rightarrow 1 - C_4H_8 + C_7H_7 \cdot$	8.9	12.2
248	$4 - C_4H_7 \cdot + C_8H_{10}$	$\rightarrow 1 - C_4H_8 + C_8H_9 \cdot$	8.9	12.2
249	$4 - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow 1 - C_4H_8 + 1 - C_4H_9 \cdot$	8.9	12.2
250	$4 - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow 1 - C_4H_8 + 2 - C_4H_9 \cdot$	8.9	12.2
251	$4 - C_4H_7 \cdot + CyC_6H_{10}$	$\rightarrow 1 - C_4H_8 + H \cdot + H_2 + C_6H_6$	8.9	12.2
252	$iso - C_4H_7 \cdot + H_2$	$\rightarrow iso - C_4H_8 + H \cdot$	9.60	23.0
253	$iso - C_4H_7 \cdot + CH_4$	$\rightarrow iso - C_4H_8 + CH_3 \cdot$	9.60	23.0
254	$iso - C_4H_7 \cdot + C_2H_4$	$\rightarrow iso - C_4H_8 + C_2H_3 \cdot$	9.60	23.0
255	$iso - C_4H_7 \cdot + C_2H_6$	$\rightarrow iso - C_4H_8 + C_2H_5 \cdot$	9.60	23.0
256	$iso - C_4H_7 \cdot + C_3H_6$	$\rightarrow iso - C_4H_8 + a - C_3H_5 \cdot$	9.60	23.0
257	$iso - C_4H_7 \cdot + C_3H_6$	$\rightarrow iso - C_4H_8 + v - C_3H_5 \cdot$	9.60	23.0
258	$iso - C_4H_7 \cdot + C_3H_8$	$\rightarrow iso - C_4H_8 + 1 - C_3H_7 \cdot$	9.60	23.0
259	$iso - C_4H_7 \cdot + C_3H_8$	$\rightarrow iso - C_4H_8 + 2 - C_3H_7 \cdot$	9.60	23.0
260	$iso - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow iso - C_4H_8 + a - C_4H_7 \cdot$	9.60	23.0
261	$iso - C_4H_7 \cdot + 1 - C_4H_8$	$\rightarrow iso - C_4H_8 + 4 - C_4H_7 \cdot$	9.60	23.0
262	$iso - C_4H_7 \cdot + 2 - C_4H_8$	$\rightarrow iso - C_4H_8 + a - C_4H_7 \cdot$	9.60	23.0
263	$iso - C_4H_7 \cdot + iso - C_4H_8$	$\rightarrow iso - C_4H_8 + iso - C_4H_7 \cdot$	9.60	23.0
264	$iso - C_4H_7 \cdot + C_5H_8$	$\rightarrow iso - C_4H_8 + H \cdot + CyC_5H_6$	9.60	23.0
265	$iso - C_4H_7 \cdot + CyC_5H_8$	$\rightarrow iso - C_4H_8 + H \cdot + CyC_5H_6$	9.60	23.0
266	$iso - C_4H_7 \cdot + CyC_5H_6$	$\rightarrow iso - C_4H_8 + CyC_5H_5 \cdot$	9.60	23.0
267	$iso - C_4H_7 \cdot + C_6H_{10}$	$\rightarrow iso - C_4H_8 + CH_3 \cdot + CyC_5H_6$	9.60	23.0
268	$iso - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow iso - C_4H_8 + CH_3 \cdot + CyC_5H_6$	9.60	23.0
269	$iso - C_4H_7 \cdot + MeCyC_5H_7$	$\rightarrow iso - C_4H_8 + H \cdot + MeCyC_5H_5$	9.60	23.0
270	$iso - C_4H_7 \cdot + MeCyC_5H_5$	$\rightarrow iso - C_4H_8 + H \cdot + C_6H_6$	9.60	23.0
271	$iso - C_4H_7 \cdot + C_7H_8$	$\rightarrow iso - C_4H_8 + C_7H_7 \cdot$	9.60	23.0
272	$iso - C_4H_7 \cdot + C_8H_{10}$	$\rightarrow iso - C_4H_8 + C_8H_9 \cdot$	9.60	23.0
273	$iso - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow iso - C_4H_8 + 1 - C_4H_9 \cdot$	9.60	23.0
274	$iso - C_4H_7 \cdot + n - C_4H_{10}$	$\rightarrow iso - C_4H_8 + 2 - C_4H_9 \cdot$	9.60	23.0
275	$iso - C_4H_7 \cdot + CyC_6H_{10}$	$\rightarrow iso - C_4H_8 + H \cdot + H_2 + C_6H_6$	9.60	23.0
276	$1 - C_4H_9 \cdot + H_2$	$\rightarrow n - C_4H_{10} + H \cdot$	8.90	14.0
277	$1 - C_4H_9 \cdot + CH_4$	$\rightarrow n - C_4H_{10} + CH_3 \cdot$	8.90	14.0
278	$1 - C_4H_9 \cdot + C_2H_4$	$\rightarrow n - C_4H_{10} + C_2H_3 \cdot$	8.90	14.0
279	$1 - C_4H_9 \cdot + C_2H_6$	$\rightarrow n - C_4H_{10} + C_2H_5 \cdot$	8.90	14.0
280	$1 - C_4H_9 \cdot + C_3H_6$	$\rightarrow n - C_4H_{10} + a - C_3H_5 \cdot$	8.90	14.0

281	$1 - C_4H_9 \cdot + C_3H_6$	$\rightarrow n - C_4H_{10} + v - C_3H_5 \cdot$	8.90	14.0
282	$1 - C_4H_9 \cdot + C_3H_8$	$\rightarrow n - C_4H_{10} + 1 - C_3H_7 \cdot$	8.90	14.0
283	$1 - C_4H_9 \cdot + C_3H_8$	$\rightarrow n - C_4H_{10} + 2 - C_3H_7 \cdot$	8.90	14.0
284	$1 - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow n - C_4H_{10} + a - C_4H_7 \cdot$	8.90	14.0
285	$1 - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow n - C_4H_{10} + 4 - C_4H_7 \cdot$	8.90	14.0
286	$1 - C_4H_9 \cdot + 2 - C_4H_8$	$\rightarrow n - C_4H_{10} + a - C_4H_7 \cdot$	8.90	14.0
287	$1 - C_4H_9 \cdot + iso - C_4H_8$	$\rightarrow n - C_4H_{10} + iso - C_4H_7 \cdot$	8.90	14.0
288	$1 - C_4H_9 \cdot + C_5H_8$	$\rightarrow n - C_4H_{10} + H \cdot + CyC_5H_6$	8.90	14.0
289	$1 - C_4H_9 \cdot + CyC_5H_8$	$\rightarrow n - C_4H_{10} + H \cdot + CyC_5H_6$	8.90	14.0
290	$1 - C_4H_9 \cdot + CyC_5H_6$	$\rightarrow n - C_4H_{10} + CyC_5H_5 \cdot$	8.90	14.0
291	$1 - C_4H_9 \cdot + C_6H_{10}$	$\rightarrow n - C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	14.0
292	$1 - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow n - C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	14.0
293	$1 - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow n - C_4H_{10} + H \cdot + MeCyC_5H_5$	8.90	14.0
294	$1 - C_4H_9 \cdot + MeCyC_5H_5$	$\rightarrow n - C_4H_{10} + H \cdot + C_6H_6$	8.90	14.0
295	$1 - C_4H_9 \cdot + C_7H_8$	$\rightarrow n - C_4H_{10} + C_7H_7 \cdot$	8.90	14.0
296	$1 - C_4H_9 \cdot + C_8H_{10}$	$\rightarrow n - C_4H_{10} + C_8H_9 \cdot$	8.90	14.0
297	$1 - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow n - C_4H_{10} + 1 - C_4H_9 \cdot$	8.90	14.0
298	$1 - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow n - C_4H_{10} + 2 - C_4H_9 \cdot$	8.90	14.0
299	$1 - C_4H_9 \cdot + CyC_6H_{10}$	$\rightarrow n - C_4H_{10} + H \cdot + H_2 + C_6H_6$	8.90	14.0
300	$iso - C_4H_9 \cdot + H_2$	$\rightarrow iso - C_4H_{10} + H \cdot$	8.90	14.0
301	$iso - C_4H_9 \cdot + CH_4$	$\rightarrow iso - C_4H_{10} + CH_3 \cdot$	8.90	14.0
302	$iso - C_4H_9 \cdot + C_2H_4$	$\rightarrow iso - C_4H_{10} + C_2H_3 \cdot$	8.90	14.0
303	$iso - C_4H_9 \cdot + C_2H_6$	$\rightarrow iso - C_4H_{10} + C_2H_5 \cdot$	8.90	14.0
304	$iso - C_4H_9 \cdot + C_3H_6$	$\rightarrow iso - C_4H_{10} + a - C_3H_5 \cdot$	8.90	14.0
305	$iso - C_4H_9 \cdot + C_3H_6$	$\rightarrow iso - C_4H_{10} + v - C_3H_5 \cdot$	8.90	14.0
306	$iso - C_4H_9 \cdot + C_3H_8$	$\rightarrow iso - C_4H_{10} + 1 - C_3H_7 \cdot$	8.90	14.0
307	$iso - C_4H_9 \cdot + C_3H_8$	$\rightarrow iso - C_4H_{10} + 2 - C_3H_7 \cdot$	8.90	14.0
308	$iso - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow iso - C_4H_{10} + a - C_4H_7 \cdot$	8.90	14.0
309	$iso - C_4H_9 \cdot + 1 - C_4H_8$	$\rightarrow iso - C_4H_{10} + 4 - C_4H_7 \cdot$	8.90	14.0
310	$iso - C_4H_9 \cdot + 2 - C_4H_8$	$\rightarrow iso - C_4H_{10} + a - C_4H_7 \cdot$	8.90	14.0
311	$iso - C_4H_9 \cdot + iso - C_4H_8$	$\rightarrow iso - C_4H_{10} + iso - C_4H_7 \cdot$	8.90	14.0
312	$iso - C_4H_9 \cdot + C_5H_8$	$\rightarrow iso - C_4H_{10} + H \cdot + CyC_5H_6$	8.90	14.0
313	$iso - C_4H_9 \cdot + CyC_5H_8$	$\rightarrow iso - C_4H_{10} + H \cdot + CyC_5H_6$	8.90	14.0
314	$iso - C_4H_9 \cdot + CyC_5H_6$	$\rightarrow iso - C_4H_{10} + CyC_5H_5 \cdot$	8.90	14.0
315	$iso - C_4H_9 \cdot + C_6H_{10}$	$\rightarrow iso - C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	14.0
316	$iso - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow iso - C_4H_{10} + CH_3 \cdot + CyC_5H_6$	8.90	14.0
317	$iso - C_4H_9 \cdot + MeCyC_5H_7$	$\rightarrow iso - C_4H_{10} + H \cdot + MeCyC_5H_5$	8.90	14.0
318	$iso - C_4H_9 \cdot + MeCyC_5H_5$	$\rightarrow iso - C_4H_{10} + H \cdot + C_6H_6$	8.90	14.0
319	$iso - C_4H_9 \cdot + C_7H_8$	$\rightarrow iso - C_4H_{10} + C_7H_7 \cdot$	8.90	14.0
320	$iso - C_4H_9 \cdot + C_8H_{10}$	$\rightarrow iso - C_4H_{10} + C_8H_9 \cdot$	8.90	14.0
321	$iso - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow iso - C_4H_{10} + 1 - C_4H_9 \cdot$	8.90	14.0
322	$iso - C_4H_9 \cdot + n - C_4H_{10}$	$\rightarrow iso - C_4H_{10} + 2 - C_4H_9 \cdot$	8.90	14.0
323	$iso - C_4H_9 \cdot + CyC_6H_{10}$	$\rightarrow iso - C_4H_{10} + H \cdot + H_2 + C_6H_6$	8.90	14.0
324	$CyC_5H_5 \cdot + H_2$	$\rightarrow CyC_5H_6 + H \cdot$	9.60	32.5
325	$CyC_5H_5 \cdot + CH_4$	$\rightarrow CyC_5H_6 + CH_3 \cdot$	9.60	32.5
326	$CyC_5H_5 \cdot + C_2H_4$	$\rightarrow CyC_5H_6 + C_2H_3 \cdot$	9.60	32.5
327	$CyC_5H_5 \cdot + C_2H_6$	$\rightarrow CyC_5H_6 + C_2H_5 \cdot$	9.60	32.5
328	$CyC_5H_5 \cdot + C_3H_6$	$\rightarrow CyC_5H_6 + a - C_3H_5 \cdot$	9.60	32.5
329	$CyC_5H_5 \cdot + C_3H_6$	$\rightarrow CyC_5H_6 + v - C_3H_5 \cdot$	9.60	32.5
330	$CyC_5H_5 \cdot + C_3H_8$	$\rightarrow CyC_5H_6 + 1 - C_3H_7 \cdot$	9.60	32.5

331	$\text{CyC}_5\text{H}_5 \cdot + \text{C}_3\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + 2 - \text{C}_3\text{H}_7 \cdot$	9.60	32.5
332	$\text{CyC}_5\text{H}_5 \cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + a - \text{C}_4\text{H}_7 \cdot$	9.60	32.5
333	$\text{CyC}_5\text{H}_5 \cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + 4 - \text{C}_4\text{H}_7 \cdot$	9.60	32.5
334	$\text{CyC}_5\text{H}_5 \cdot + 2 - \text{C}_4\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + a - \text{C}_4\text{H}_7 \cdot$	9.60	32.5
335	$\text{CyC}_5\text{H}_5 \cdot + \text{iso} - \text{C}_4\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{iso} - \text{C}_4\text{H}_7 \cdot$	9.60	32.5
336	$\text{CyC}_5\text{H}_5 \cdot + \text{C}_5\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot + \text{CyC}_5\text{H}_6$	9.60	32.5
337	$\text{CyC}_5\text{H}_5 \cdot + \text{CyC}_5\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot + \text{CyC}_5\text{H}_6$	9.60	32.5
338	$\text{CyC}_5\text{H}_5 \cdot + \text{CyC}_5\text{H}_6$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{CyC}_5\text{H}_5 \cdot$	9.60	32.5
339	$\text{CyC}_5\text{H}_5 \cdot + \text{C}_6\text{H}_{10}$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{CH}_3 \cdot + \text{CyC}_5\text{H}_6$	9.60	32.5
340	$\text{CyC}_5\text{H}_5 \cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{CH}_3 \cdot + \text{CyC}_5\text{H}_6$	9.60	32.5
341	$\text{CyC}_5\text{H}_5 \cdot + \text{MeCyC}_5\text{H}_7$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot + \text{MeCyC}_5\text{H}_5$	9.60	32.5
342	$\text{CyC}_5\text{H}_5 \cdot + \text{MeCyC}_5\text{H}_5$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot + \text{C}_6\text{H}_6$	9.60	32.5
343	$\text{CyC}_5\text{H}_5 \cdot + \text{C}_7\text{H}_8$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{C}_7\text{H}_7 \cdot$	9.60	32.5
344	$\text{CyC}_5\text{H}_5 \cdot + \text{C}_8\text{H}_{10}$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{C}_8\text{H}_9 \cdot$	9.60	32.5
345	$\text{CyC}_5\text{H}_5 \cdot + n - \text{C}_4\text{H}_{10}$	$\rightarrow \text{CyC}_5\text{H}_6 + 1 - \text{C}_4\text{H}_9 \cdot$	9.60	32.5
346	$\text{CyC}_5\text{H}_5 \cdot + n - \text{C}_4\text{H}_{10}$	$\rightarrow \text{CyC}_5\text{H}_6 + 2 - \text{C}_4\text{H}_9 \cdot$	9.60	32.5
347	$\text{CyC}_5\text{H}_5 \cdot + \text{CyC}_6\text{H}_{10}$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot + \text{H}_2 + \text{C}_6\text{H}_6$	9.60	32.5

### A.3 Radical-addition reactions

			$\log_{10} k_{\infty}$	$E_A$ [ $\frac{\text{kcal}}{\text{mol}}$ ]
348	$\text{H} \cdot + \text{C}_2\text{H}_2 + \text{T}$	$\rightarrow \text{C}_2\text{H}_3 \cdot + \text{T}$	9.00	-10.0
349	$\text{H} \cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{C}_2\text{H}_5 \cdot$	11.0	2.0
350	$\text{H} \cdot + \text{C}_3\text{H}_4^{\equiv}$	$\rightarrow a - \text{C}_3\text{H}_5 \cdot$	10.54	2.0
351	$\text{H} \cdot + \text{C}_3\text{H}_4^{\equiv}$	$\rightarrow v - \text{C}_3\text{H}_5 \cdot$	10.54	2.0
352	$\text{H} \cdot + \text{C}_3\text{H}_6$	$\rightarrow 1 - \text{C}_3\text{H}_7 \cdot$	10.64	2.0
353	$\text{H} \cdot + \text{C}_3\text{H}_6$	$\rightarrow 2 - \text{C}_3\text{H}_7 \cdot$	10.64	2.0
354	$\text{H} \cdot + \text{C}_4\text{H}_6$	$\rightarrow a - \text{C}_4\text{H}_7 \cdot$	11.08	1.9
355	$\text{H} \cdot + \text{C}_4\text{H}_6$	$\rightarrow 4 - \text{C}_4\text{H}_7 \cdot$	10.61	2.0
356	$\text{H} \cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow 1 - \text{C}_4\text{H}_9 \cdot$	10.40	2.0
357	$\text{H} \cdot + 1 - \text{C}_4\text{H}_8$	$\rightarrow 2 - \text{C}_4\text{H}_9 \cdot$	10.88	2.0
358	$\text{H} \cdot + 2 - \text{C}_4\text{H}_8$	$\rightarrow 2 - \text{C}_4\text{H}_9 \cdot$	11.00	2.5
359	$\text{H} \cdot + \text{iso} - \text{C}_4\text{H}_8$	$\rightarrow \text{iso} - \text{C}_4\text{H}_9 \cdot$	11.00	2.0
360	$\text{H} \cdot + \text{C}_7\text{H}_8$	$\rightarrow \text{C}_6\text{H}_6 + \text{CH}_3 \cdot$	10.70	5.0
361	$\text{H} \cdot + \text{C}_8\text{H}_{10}$	$\rightarrow \text{C}_7\text{H}_8 + \text{CH}_3 \cdot$	10.90	5.0
362	$\text{H} \cdot + \text{C}_8\text{H}_8$	$\rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_3 \cdot$	11.48	12.0
363	$\text{CH}_3 \cdot + \text{C}_3\text{H}_6$	$\rightarrow 1 - \text{C}_3\text{H}_7 \cdot$	8.48	7.6
364	$\text{CH}_3 \cdot + \text{C}_3\text{H}_6$	$\rightarrow 2 - \text{C}_4\text{H}_9 \cdot$	8.60	7.6
365	$\text{CH}_3 \cdot + \text{C}_3\text{H}_6$	$\rightarrow \text{iso} - \text{C}_4\text{H}_9 \cdot$	8.30	7.6
366	$\text{C}_2\text{H}_3 \cdot + \text{C}_2\text{H}_4$	$\rightarrow 4 - \text{C}_4\text{H}_7 \cdot$	8.55	6.0
367	$\text{C}_2\text{H}_3 \cdot + \text{C}_3\text{H}_6$	$\rightarrow \frac{1}{2} (\text{CH}_3 \cdot + \text{C}_4\text{H}_6) + \frac{1}{2} (\text{H} \cdot + \text{C}_5\text{H}_8)$	8.20	6.0
368	$\text{C}_2\text{H}_3 \cdot + \text{C}_4\text{H}_6$	$\rightarrow \frac{3}{4} (\text{CyC}_5\text{H}_6 + \text{CH}_3 \cdot) + \frac{1}{4} (\text{H} \cdot + \text{H}_2 + \text{C}_6\text{H}_6)$	8.64	5.0
369	$\text{C}_2\text{H}_3 \cdot + \text{C}_6\text{H}_6$	$\rightarrow \text{C}_8\text{H}_8 + \text{H} \cdot$	8.40	6.0
370	$\text{C}_2\text{H}_3 \cdot + \text{C}_8\text{H}_8$	$\rightarrow \text{C}_9^+$	8.70	5.0
371	$\text{C}_2\text{H}_3 \cdot + \text{CyC}_5\text{H}_6$	$\rightarrow \text{C}_7\text{H}_8 + \text{H} \cdot$	8.60	5.0
372	$\text{C}_2\text{H}_5 \cdot + \text{C}_2\text{H}_4$	$\rightarrow 1 - \text{C}_4\text{H}_9 \cdot$	8.30	7.6
373	$a - \text{C}_3\text{H}_5 \cdot + \text{C}_2\text{H}_2$	$\rightarrow \text{CyC}_5\text{H}_6 + \text{H} \cdot$	8.30	13.0
374	$a - \text{C}_3\text{H}_5 \cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{C}_5\text{H}_8 + \text{H} \cdot$	7.82	21.5
375	$a - \text{C}_3\text{H}_5 \cdot + \text{C}_2\text{H}_4$	$\rightarrow \text{CyC}_5\text{H}_8 + \text{H} \cdot$	7.08	12.5
376	$a - \text{C}_3\text{H}_5 \cdot + \text{C}_3\text{H}_6$	$\rightarrow 4 - \text{C}_4\text{H}_7 \cdot + \text{C}_2\text{H}_4$	7.88	21.5

377	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_2H_5 \cdot + C_4H_6$	7.78	21.5
378	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow CH_3 \cdot + CyC_5H_8$	7.60	21.5
379	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow H \cdot + C_6H_{10}$	7.88	21.5
380	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow MeCyC_5H_7 + H \cdot$	6.57	12.5
381	$a - C_3H_5 \cdot + C_3H_6$	$\rightarrow C_6H_{10} + H \cdot$	6.57	12.5
382	$a - C_3H_5 \cdot + C_4H_6$	$\rightarrow C_2H_5 \cdot + CyC_5H_6$	6.01	5.0
383	$a - C_3H_5 \cdot + C_4H_6$	$\rightarrow CH_3 \cdot + H_2 + C_6H_6$	6.38	5.0
384	$a - C_3H_5 \cdot + CyC_5H_6$	$\rightarrow CH_3 \cdot + C_7H_8$	8.65	14.5
385	$a - C_3H_5 \cdot + C_6H_6$	$\rightarrow C_9^+$	8.78	25.0
386	$a - C_3H_5 \cdot + C_8H_8$	$\rightarrow C_9^+$	7.08	12.0
387	$a - C_4H_7 \cdot + C_2H_4$	$\rightarrow CH_3 \cdot + CyC_5H_8$	8.48	13.0

#### A.4 Radical-decomposition reactions

		$\log_{10} k_{\infty}$	$E_A \left[ \frac{kcal}{mol} \right]$
388	$C_2H_3 \cdot + T \rightarrow C_2H_2 + H \cdot + T$	11.90	29.7
389	$C_2H_5 \cdot \rightarrow C_2H_4 + H \cdot$	13.90	41.0
390	$a - C_3H_5 \cdot \rightarrow C_3H_4^{\equiv} + H \cdot$	12.95	59.0
391	$v - C_3H_5 \cdot \rightarrow C_3H_4^{\equiv} + H \cdot$	12.15	37.5
392	$v - C_3H_5 \cdot \rightarrow C_2H_2 + CH_3 \cdot$	12.20	37.5
393	$1 - C_3H_7 \cdot \rightarrow C_2H_4 + CH_3 \cdot$	13.70	34.0
394	$1 - C_3H_7 \cdot \rightarrow C_3H_6 + H \cdot$	14.30	39.0
395	$2 - C_3H_7 \cdot \rightarrow C_3H_6 + H \cdot$	14.30	43.0
396	$4 - C_4H_7 \cdot \rightarrow C_2H_4 + C_2H_3 \cdot$	14.30	39.5
397	$4 - C_4H_7 \cdot \rightarrow C_4H_6 + H \cdot$	13.00	34.0
398	$a - C_4H_7 \cdot \rightarrow C_4H_6 + H \cdot$	14.00	49.0
399	$iso - C_4H_7 \cdot \rightarrow C_3H_4^{\equiv} + CH_3 \cdot$	14.08	55.0
400	$1 - C_4H_9 \cdot \rightarrow 1 - C_4H_8 + H \cdot$	14.11	39.0
401	$1 - C_4H_9 \cdot \rightarrow C_2H_4 + C_2H_5 \cdot$	14.18	31.0
402	$2 - C_4H_9 \cdot \rightarrow 1 - C_4H_8 + H \cdot$	13.70	41.0
403	$2 - C_4H_9 \cdot \rightarrow 2 - C_4H_8 + H \cdot$	14.00	41.0
404	$2 - C_4H_9 \cdot \rightarrow C_3H_6 + CH_3 \cdot$	14.00	34.0
405	$iso - C_4H_9 \cdot \rightarrow iso - C_4H_8 + H \cdot$	14.00	38.0
406	$iso - C_4H_9 \cdot \rightarrow C_3H_6 + CH_3 \cdot$	14.30	34.0

#### A.5 Radical-isomerization reactions

		$\log_{10} k_{\infty}$	$E_A \left[ \frac{kcal}{mol} \right]$
407	$1 - C_3H_7 \cdot \rightarrow 2 - C_3H_7 \cdot$	12.40	34.0
408	$2 - C_3H_7 \cdot \rightarrow 1 - C_3H_7 \cdot$	13.00	38.0
409	$a - C_4H_7 \cdot \rightarrow 4 - C_4H_7 \cdot$	13.44	49.0
410	$4 - C_4H_7 \cdot \rightarrow a - C_4H_7 \cdot$	12.70	35.0

#### A.6 Chain-termination reactions

		$\log_{10} k_{\infty}$	$E_A \left[ \frac{kcal}{mol} \right]$
411	$2CH_3 \cdot \rightarrow C_2H_6$	10.34	0.
412	$CH_3 \cdot + C_2H_5 \cdot \rightarrow C_3H_8$	10.00	0.

413	$\text{CH}_3 \cdot + \text{a} - \text{C}_3\text{H}_5 \cdot$	$\rightarrow$	$1 - \text{C}_4\text{H}_8$	9.85	0.
414	$2\text{a} - \text{C}_3\text{H}_5 \cdot$	$\rightarrow$	Diallyl	8.70	0.
415	$\text{C}_2\text{H}_5 \cdot + \text{C}_2\text{H}_5 \cdot$	$\rightarrow$	$n - \text{C}_4\text{H}_{10}$	9.30	0.

## A.7 Molecular reactions

			$\log_{10} k_{\infty}$	$E_A$ [ $\frac{\text{kcal}}{\text{mol}}$ ]	
416	$\text{C}_2\text{H}_6$	$\rightarrow$	$\text{C}_2\text{H}_4 + \text{H}_2$	13.90	71.0
417	$\text{C}_2\text{H}_4 + \text{H}_2$	$\rightarrow$	$\text{C}_2\text{H}_6$	8.90	38.0
418	$\text{C}_3\text{H}_4^{\equiv}$	$\rightarrow$	$\text{C}_3\text{H}_4^{\equiv}$	13.50	63.0
419	$\text{C}_3\text{H}_4^{\equiv}$	$\rightarrow$	$\text{C}_3\text{H}_4^{\equiv}$	13.2	61.5
420	$\text{C}_3\text{H}_8$	$\rightarrow$	$\text{C}_3\text{H}_6 + \text{H}_2$	13.7	70.0
421	$\text{C}_3\text{H}_6 + \text{H}_2$	$\rightarrow$	$\text{C}_3\text{H}_8$	8.90	38.0
422	$1 - \text{C}_4\text{H}_8$	$\rightarrow$	$2 - \text{C}_4\text{H}_8$	12.35	60.0
423	$2 - \text{C}_4\text{H}_8$	$\rightarrow$	$1 - \text{C}_4\text{H}_8$	12.29	62.0
424	$\text{CyC}_5\text{H}_8$	$\rightarrow$	$\text{CyC}_5\text{H}_6 + \text{H}_2$	13.30	58.0
425	Diallyl	$\rightarrow$	$2\text{H}_2 + \text{C}_6\text{H}_6$	13.78	59.0
426	$\text{Me} - \text{CyC}_5\text{H}_7$	$\rightarrow$	$\text{Me} - \text{CyC}_5\text{H}_5 + \text{H}_2$	13.68	64.0
427	$\text{Me} - \text{CyC}_5\text{H}_7$	$\rightarrow$	$\text{C}_6\text{H}_{10}$	13.86	64.0
428	$\text{CyC}_5\text{H}_6 + \text{C}_2\text{H}_2$	$\rightarrow$	$\text{C}_7\text{H}_8$	8.00	21.5
429	$\text{C}_4\text{H}_6 + \text{C}_2\text{H}_2$	$\rightarrow$	$\text{C}_6\text{H}_6 + \text{H}_2$	8.18	22.5
430	$\text{C}_4\text{H}_6 + \text{C}_3\text{H}_4^{\equiv}$	$\rightarrow$	$\text{C}_7\text{H}_8 + \text{H}_2$	7.87	22.5
431	$\text{CyC}_5\text{H}_6 + \text{C}_3\text{H}_4^{\equiv}$	$\rightarrow$	$\text{C}_8\text{H}_{10}$	8.00	21.5
432	$\text{C}_2\text{H}_4 + \text{C}_4\text{H}_6$	$\rightarrow$	$\text{CyC}_6\text{H}_{10}$	7.48	26.5
433	$\text{CyC}_6\text{H}_{10}$	$\rightarrow$	$\frac{9}{10} (\text{C}_2\text{H}_4 + \text{C}_4\text{H}_6) + \frac{1}{10} (2\text{H}_2 + \text{C}_6\text{H}_6)$	15.04	66.7

## Appendix B

### Components

no.	chemical formula	wt% in feed A [DR83]	wt% in feed B [DR83]
<b>C<sub>1</sub>-chains</b>			
1	$CH_3\cdot$		
2	$CH_4$		
<b>C<sub>2</sub>-chains</b>			
3	$C_2H_2$		
4	$C_2H_3\cdot$		
5	$C_2H_4$	0.75	
6	$C_2H_5\cdot$		
7	$C_2H_6$	99.25	0.15
<b>C<sub>3</sub>-chains</b>			
8	$C_3H_4^{==}$		
9	$C_3H_4^{\equiv}$		
10	$a - C_3H_5\cdot$		
11	$v - C_3H_5\cdot$		
12	$C_3H_6$		
13	$1 - C_3H_7\cdot$		
14	$2 - C_3H_7\cdot$		
15	$C_3H_8$		86.40
<b>C<sub>4</sub>-chains</b>			
16	$C_4H_6$		
17	$a - C_4H_7\cdot$		
18	$iso - C_4H_7\cdot$		
19	$4 - C_4H_7\cdot$		
20	$1 - C_4H_8$		
21	$2 - C_4H_8$		
22	$iso - C_4H_8$		
23	$1 - C_4H_9\cdot$		
24	$2 - C_4H_9\cdot$		
25	$iso - C_4H_9\cdot$		
26	$n - C_4H_{10}$		5.72
27	$iso - C_4H_{10}$		2.51
<b>C<sub>5</sub>-chains</b>			
28	$CyC_5H_5\cdot$		
29	$CyC_5H_6$		
30	$C_5H_8$		
31	$CyC_5H_8$		
<b>C<sub>6</sub>-chains</b>			
32	$Me - CyC_5H_5$		
33	$Me - CyC_5H_7$		

---

34	$C_6H_6$		
35	$C_6H_{10}$		
36	$CyC_6H_{10}$		
37	<i>Diallyl</i>		
<b>C<sub>7</sub>-chains</b>			
38	$C_7H_7\cdot$		
39	$C_7H_8$		
<b>C<sub>8</sub>-chains</b>			
40	$C_8H_8$		
41	$C_8H_9\cdot$		
42	$C_8H_{10}$		
<b>C<sub>9</sub>+chains</b>			
43	$C_9H_{11}$		
44	$C_{10}H_{11}$		
45	$C_{11}H_{13}$		
<b>others</b>			
46	$H\cdot$		
47	$H_2$		
48	$H_2O$	steam	steam

## Appendix C

### Composition of Naphtha

Table C.1: Naphtha Sample Total Raffinerie 23.02.2007

	Unit	C3	C4	C5	C6	C7	C8	C9	C10	C11	Poly	sum
Aromatics	Vol%	0	0	0	0.83	0.57	0.73	0.39	0.00	0.00	0	2.52
i-Olefines	Vol%	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0	0.45
i-Paraffines	Vol%	0.00	0.23	6.87	12.84	8.58	2.83	1.92	0.57	0.00	0	33.84
Naphthenes	Vol%	0.00	0.00	1.28	13.40	6.57	2.99	1.67	0.00	0.00	0	25.92
n-Olefines	Vol%	0.00	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.35
n-Paraffines	Vol%	0.00	3.89	10.41	15.53	3.75	1.97	0.89	0.47	0.00	0	63.93
Aromatics	Weight%	0	0	0	1.06	0.71	0.92	0.49	0.00	0.00	0	3.19
i-Olefines	Weight%	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0	0.45
i-Paraffines	Weight%	0.00	0.19	6.10	12.23	8.53	2.90	2.03	0.61	0.00	0	32.59
Naphthenes	Weight%	0.00	0.00	1.38	14.83	7.28	3.36	1.90	0.00	0.00	0	28.75
n-Olefines	Weight%	0.00	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.31
n-Paraffines	Weight%	0.00	3.27	9.44	14.84	3.72	2.00	0.93	0.50	0.00	0	34.70

Table C.3: Naphtha Sample Shell Raffinerie 26.11.2008

	Unit	C4	C5	C6	C7	C8	C9	C10	C11	C12+	Poly	sum
Aromatics	Weight%	0	0	1.36	2.03	1.43	1.33	0.18	0	0.08	0	6.41
i-Olefines	Weight%	0	0.08	0.02	0.01	0	0.02	0	0.02	0	0	0.14
i-Paraffines	Weight%	0.31	11.85	7.76	5.51	4.76	2.95	1.33	0.08	0.23	0	34.79
Naphthenes	Weight%	0	1.09	5.93	8.05	6.77	3.64	1.04	0	0	0.07	26.60
n-Olefines	Weight%	0.03	0.08	0	0.01	0	0.02	0	0.03	0	0	0.16
n-Paraffines	Weight%	2.93	13.93	6.47	3.78	2.40	1.42	0.75	0.22	0	0	63.96
Aromatics	Vol%	0	0	1.07	1.62	1.14	1.06	0.14	0	0.07	0	5.10
i-Olefines	Vol%	0	0.08	0.02	0.01	0	0.02	0	0.02	0	0	0.15
i-Paraffines	Vol%	0.38	13.18	8.17	5.58	4.68	2.83	1.26	0.08	0.24	0	36.41
Naphthenes	Vol%	0	1.01	5.43	7.37	6.05	3.21	0.89	0	0	0.06	24.02
n-Olefines	Vol%	0.03	0.08	0	0.01	0	0.01	0	0.02	0	0	0.17
n-Paraffines	Vol%	3.50	15.40	6.77	3.83	2.37	1.37	0.71	0.21	0	0	34.16

## Appendix D

### Matlab®functions

#### D.1 main function

```

1 function [] = steamcracker_main(varargin)
2 [...]
3 opts = varargin;
4 [...]
5 %-----
6 % 2. Set some parameters
7 %-----
8
9 % system parameters
10 p.T_in = 873; %inlet temperature [K]
11 p.x_steam = 0.5; %steam mass-fraction [-]
12 [...]
13 %-----
14 % 3. call functions to load matrices (for reactions and components)
15 %-----
16
17 % matrix of stoichiometric coefficients
18 nu_complete = build_nu();
19
20 % reduce this matrix
21 nu = nu_complete(:,p.red_start:p.red_end);
22
23 % find parameters of the reaction scheme
24 p.num_reac = length(nu(1,:));
25 p.num_com = length(nu(:,1));
26 p.nu=nu;
27
28 % component - element matrix
29 beta = build_beta();
30
31 % calculate vector of molar masses
32 p.M_tilde = p.M * beta'.*1000; %[kg/mol]
33
34 % matrix of kinetic constants
35 ek_complete = build_ek();
36
37 % reduce this matrix
38 p.ek = ek_complete(p.red_start:p.red_end,:);
39 % recalculate freq.factor in [m^3/(mol s)]
40 p.ek_norm = [10.^(p.ek(:,1))./1000 p.ek(:,2)];
41
42 % matrix for standard formation enthalpies
43 p.bh = build_bh;

```

```

44
45 % build reaction enthalpies
46 p.rh = zeros(1,433);
47 for i=1:length(nu(1,:))
48     p.rh(i)=nu(1:p.num_com-1,i)'*p.bh;
49 end
50
51 [...]
52
53 %-----
54 % 5. set boundary and initial conditions
55 %-----
56
57 if p.feed_config == 1
58     x0 = boundary_c(p,p.feed);
59 else
60     x0 = boundary_fractions_c(p,p.feed);
61 end
62
63 % feed temperature l.a. the top
64 if p.config == 1
65     T_in = p.T_mean;
66 else
67     T_in = p.T_in;
68 end
69
70 %-----
71 % 6. ODE call
72 %-----
73
74 % start conditions
75 x0=[x0 ; T_in];
76
77 [l,x] = ode15s(@steamcracker_ode,[0 p.L],x0,[],p);
78
79 %-----
80 % 7. Analysis
81 %-----
82
83 % Calculations for Analysis
84 % =====
85 % split vector
86 w = x(:,1:p.num_com);
87 T = x(:,p.num_com+1);
88
89 % calculate total fractions for different fractions in each l-step
90 % calculate sums
91 for i=1:length(l)
92     sumC1(i,1) = sum(w(i,1:2));
93     [...]
94 end
95 sumMatrix = [sumC1,sumC2,sumC3,sumC4,sumC5,sumC6,sumC7,sumC8,sumC9,sumrest];
96
97 % calculate mean chain lengths for each l-step
98 for i=1:length(l)
99     mean_length(i)=sumMatrix(i,[a:b])*[a:b]';
100 end

```

```

101
102
103 % Different Plots
104 % =====
105
106 [...]

```

## D.2 ode function

```

1 function [xprime] = steamcracker_ode(l,x,p)
2
3 % split vector
4 w = x(1:p.num_com);
5 T = x(p.num_com+1);
6
7 %-----
8 % w --> c
9 %-----
10
11 c(1:p.num_com,1) = w.*(p.rho_tot)./p.M_tilde'; %[mol/m^3]
12
13
14 if p.config == 1
15     T_arr = p.T_mean;
16 else
17     T_arr = T;
18 end
19
20 %-----
21 % calculate component mass balance
22 %-----
23
24 % prefactor
25
26 prefactor = p.M_tilde'./(p.v.*p.rho_tot);
27
28 % arrhenius k(T)
29 arrhenius = (p.ek_norm(:,1)).* exp(-p.ek(:,2)./(p.R_cal.*T_arr));
30
31 % reaction rates
32 r_j      = arrhenius.*c(p.num_ed(:,1)).^abs(p.arr_ed(:,1)).*...
33           c(p.num_ed(:,2)).^abs(p.arr_ed(:,2)); %[mol/(s m^3)]
34
35 % derivative of w
36 wprime   = prefactor.*(p.nu*r_j); % in [(kg comp) / (kg m)]
37
38 %-----
39 % energy balance
40 %-----
41
42 if p.config == 1
43     Tprime = 0;
44 else
45     % calculate energy balance
46     % prefactor

```

```
47 c_p = build_cp(T,p);
48 prefactor_EB = p.v*c'*c_p;
49
50
51 % heat transport through the wall
52 if p.config == 2
53     heat_transport = 0;
54 elseif p.config == 3
55     heat_transport = p.k/p.V*p.A*(p.T_wall-T);
56 end
57
58 % heat of reaction
59 heat_reac = p.rh*r_j;
60 %heat_reac = 0;
61 % calculate Tprime
62 Tprime = 1/prefactor_EB * ( heat_transport - heat_reac );
63 end
64
65 xprime=[wprime ; Tprime];
```

### D.3 check function

```
1 function [x]= check_mb()
2
3 nu = build_nu;
4 beta = build_beta;
5
6 ch_C = nu'*beta(:,2)
7
8 k = 1;
9 for j = 1:1:length(ch_C)
10     if ch_C(j) == 0
11         else
12             x(k) = j;
13             k = k+1;
14         end
15     end
```

---

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