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Single-Event MicroKinetics for coke formation in catalytic cracking

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Abstract

A Single-Event MicroKinetic model taking into account coke formation based on elementary steps has been developed for the catalytic cracking of hydrocarbons. Coke is proposed to be formed out of coke precursors. Both coke precursors and coke formation are accounted for in terms of the same families of elementary steps as those involved in the cracking process. The coke precursors are defined as three-ring aromatic molecules. The actual and critical step for coke formation is considered to be the alkylation of coke precursors that are present in the feedstock or that are formed during the catalytic cracking.

The inclusion of coke precursors formation in the reaction network leads to an important expansion of the network. Appropriate rules are defined to keep the size of the network within tractable limits. The rate equations for the initial coke formation do not contain supplementary kinetic parameters. The only extra parameter required to be determined from experimental coking data is the average molecular mass of the coke. The developed model is implemented in a simulator of an industrial FCC riser-reactor. The calculated product and coke yield profiles are typical for industrial practice.

Keywords: Catalytic cracking; Coke; Single-Event MicroKinetics (SEMK); Coke precursors; Elementary reactions; Alkylation

1. Introduction

The catalytic cracking of heavy petroleum fractions is one of the key processes in the refining industry. It converts high boiling point feedstocks (gas oils) with low commercial value to high-value products such as naphtha, LP Gas and diesel [1]. From 30 to 40 vol% of the gasoline consumed around the world is produced via this process [2]. Light olefins contained in LP Gas produced during catalytic cracking are widely used for the production of synthetic gasoline and oxygenated octane boosters [3]. In catalytic cracking, a monofunctional acid catalyst is used. It is typically composed of 20–40 wt% of faujasite Y-zeolite dispersed in an amorphous matrix composed by silica-alumina, binder and natural clay. The catalyst formulation, i.e., zeolite type and/or matrix activity, has an important effect on the product yields [4].

During the catalytic cracking process a significant portion of the feedstock is converted into carbonaceous deposits, i.e., coke, on the catalyst. Coke formation leads to deactivation of the catalyst by poisoning of the acid sites and by blocking of the pores [5]. Coke deposition on the cracking catalyst is the main cause of catalyst deactivation. At industrial level, an excessive amount of coke not only leads to the formation of undesired reaction products but also to a lower feedstock conversion due to the decrease in the catalyst circulation for compensating the high regenerator temperatures. Nevertheless, coke is necessary for the process since its combustion in the regenerator provides the necessary heat for feedstock vaporization and for the endothermic cracking reactions [6].

The nature of the hydrocarbons in the feedstock, e.g., aromatic, naphthenic or paraffinic, the properties of the

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Nomenclature

C_C	total coke content (wt%)
C_s	coke formed by site coverage (wt%)
$C_{R_1^+}$	Concentration of carbenium ion $R_1{}^+$
F_g^o	mass flow of feedstock at the riser inlet (kg s^{-1})
HCO	heavy cycle oil
$\tilde{k}$	single-event rate coefficient (kmol $(kg_{cat}\ s)^{-1}$ or kmol $(kg_{cat}\ s\ kPa)^{-1}$)
k	elementary step rate coefficient (kmol $(kg_{cat}\ s)^{-1}$ or kmol $(kg_{cat}\ s\ kPa)^{-1}$)
$K_{(O_1;O_2)}$	modified equilibrium coefficient of the isomerization reaction between O_1 and O_2 (without global symmetry number)
$K_{(CP_i+O_j \leftrightarrow CP\_alk_{ij})}$	equilibrium coefficient for the alkylation of a coke precursor with an olefin leading to an alkylated coke precursor
LC	lumping coefficient
LCO	light cycle oil
L_i	lump i
LP Gas	liquefied petroleum gas
MW_C	average molecular mass of coke
$(n_e)_{step}$	number of single events (of elementary step)
P_{olef}	partial pressure of olefins (kPa)
P_{L_i}	partial pressure of lump i (kPa)
r_C^o	initial coking reaction rate (kg $(kg\ s)^{-1}$)
T	temperature (K)
VGO	vacuum gas oil
w_i	product yield of lump i along the riser ($kg_i\ (kg_{feedstock})^{-1}$)
z	riser position (m)

Greek symbols

α_i	deactivation constant of the elementary reaction family i ($wt\%^{-1}$)
ρ_{cat}	catalyst density (kg m^{-3})
ε	reactor void fraction
Φ_k	deactivation function of the elementary reaction family k
$\sigma_{gl,r}$	global symmetry of the reactant
$\sigma_{gl,\#}$	global symmetry of the transition state
Ω_r	reactor transversal section (m^2)
θ	hydrocarbons residence time (s)
θ_B^+	fraction of catalyst acid sites covered by carbenium ions

Subscripts

β	β-scission
alk_side	alkylation side chain
alk_nucl	alkylation aromatic nucleus
carb	carbenium ions
cat	catalyst
CP	coke precursor
cyclis	cyclization
dep	deprotonation
dep_c	deprotonation of cyclic or cyclic-aromatic carbeniun ions
dealk	dealkylation
disp	disproportionation
endβ	endocyclic beta scission of cyclic or cyclic-aromatic carbenium ions
endprot	protolytic cracking of cyclic or cyclic-aromatic hydrocarbons
habst	hydride abstraction
htf	hydride transfer
htf_c	hydride transfer of a cyclic hydrocarbon
isom	isomerization
olef	alkenes
prot	protonation
protol	protolytic scission
prot_c	protonation of a cyclic of aromatic cyclic hydrocarbon
par	alkanes
aro	aromatic
daro	diaromatic
taro	triaromatic

catalyst, e.g., total acid site concentration, acid strength of the sites and pore structure, and the operation conditions, e.g., pressure and especially temperature, have an important effect on the nature of coke and on the rate of coke formation [7]. The reaction temperature has been reported to strongly affect the coke composition [7,8]. In industrial practice, where catalytic cracking is performed above 773 K, the coke formed has a mainly polyaromatic character regardless the feedstock composition.

The coke present on the catalyst leaving the industrial riser-reactor may have different origins and, consequently, can be classified in different categories, e.g., thermal, contaminant, non-stripped hydrocarbons and catalytic coke [6,9,10]. Catalytic coke is the one which is basically formed in the zeolitic part of the catalyst and contributes to practically 50 wt% of the final coke. As a result, the accurate prediction of catalytic coke formation is an indispensable part of a simulation model for an industrial riser-reactor for catalytic cracking.

1.1. Single-Event MicroKinetics: an overview

Models for the simulation of the catalytic cracking process represent a powerful tool for evaluating operating strategies and engineering design optimization. Kinetic models using drastic lumping were widely used initially. Later on, those models have been gradually replaced by more sophisticated models considering the underlying chemistry of the cracking process [5].

Single-Event MicroKinetics (SEMK) accounts for the detailed reaction network in catalytic cracking based on the classical carbenium ion chemistry occurring on the Brönsted acid sites of zeolitic catalysts [11]. It has the advantage over other models that it uses feedstock independent rate coefficients, which has a paramount importance considering the continuous variation in the composition of catalytic cracking feedstocks [12]. Moreover, single-event kinetic parameters can be estimated through the cracking of relatively simple and representative model molecules at relevant catalytic cracking operation conditions and, hence, analytical problems can be avoided.

During the cracking of hydrocarbons a huge number of reactions take place; however, the elementary steps can be classified into a limited number of reaction families, e.g., (de)protonations, beta-scissions, alkylations, isomerizations, etc.

Within a reaction family the rate coefficients are assumed to depend only on the type of the carbenium ions involved as reactant and product and on the global symmetry number of the reactant and the transition state species. The global symmetry numbers can be extracted from the rate coefficient and calculated separately, leading to the so-called single-event rate coefficient, $\tilde{k}$, which only depends on the reaction family and the type of the carbenium ions involved [13]:

$$k = \frac{\sigma_{\mathrm{gl}}^{\mathrm{react}}}{\sigma_{\mathrm{gl}}^{\neq}} \tilde{k} \tag{1}$$

The ratio of the global symmetry number of the reactant, $\sigma_{\mathrm{gl}}^{\mathrm{reac}}$, to the transition state, $\sigma_{\mathrm{gl}}^{\neq}$, is known as the number of single events, n_{e}.

In SEMK, the carbenium ion stability is assumed to only depend on its type, i.e., the number of alkyl substituents on the carbon atom bearing the charge. The model takes into account all possible secondary and tertiary carbenium ions. Primary carbenium ions are only considered as reaction product of protolytic cracking of saturated hydrocarbons. Methyl ions are not considered in the reaction network. According to the above assumptions the 200,459 elementary steps in the *n*-dodecane catalytic cracking network can be described using 48 single-event kinetic parameters. More specifically for the reaction family of the beta-scissions four single-event parameters are considered, i.e., $\tilde{k}_{\beta}(s;s)$, $\tilde{k}_{\beta}(s;t)$, $\tilde{k}_{\beta}(t;s)$ and $\tilde{k}_{\beta}(t;t)$ for the description of 426 elementary reactions. The carbenium ion type, either secondary or tertiary, is indicated between brackets. The reaction rate of the beta-scission of a secondary carbenium (R_1^+) leading to a tertiary carbenium ion (R_2^+) and the corresponding olefin O, can be expressed by:

$$r_{\beta}(\mathrm{R}_1^+ \rightarrow \mathrm{R}_2^+ + \mathrm{O}) = n_{\mathrm{e}} \tilde{k}_{\beta}(s;t) C_{\mathrm{R}_1^+} \tag{2}$$

SEMK are one of the most advanced methods to describe kinetics in catalytic cracking. At present SEMK for catalytic cracking have been based on initial reaction rates where coke formation has not been accounted for [14]. The formation of coke and its deactivation effect are a very important issue to be addressed while modelling catalytic cracking. A combination of SEMK rate equations for the hydrocarbon conversion and global rate equations to account for the effect of coke on the catalyst activity and selectivity has been recently used [11]. The present work deals with the development of a fundamental methodology for catalytic coke formation starting from coke precursors whose formation is fully described in terms of the same elementary steps as those involved in the cracking of hydrocarbons. Other deactivation mechanisms, i.e., non catalytic coke, metal contamination, etc, are not accounted for, cf. supra. A similar methodology has already been applied for modeling coke formation in a fundamental way [15]. However, some global reactions were still present in this model, e.g., aromatizations, and some relevant elementary reactions, e.g., cyclization of acyclic species and nucleus alkylations of (poly)aromatics have not been accounted for. In addition no explicit distinction was made between coke precursors and coke, cf. infra.

Rather than focusing on the accurate simulation of an industrial riser this paper intends to outline the principles on which this model is based and to show the feasibility of the developed methodology by its implementation in a computer code for the simulation of an industrial FCC riser-reactor.

2. Coke precursors description according to SEMK principles

Apart from the main cracking reactions in catalytic cracking an important number of other elementary reactions, such as protolytic scission, (de)protonation, isomerizations (i.e., hydride-shift, alkyl-shift and pcp-branching), hydride transfer and alkylation, also occur [14,16].

Several authors have studied the formation of coke during the catalytic cracking of pure hydrocarbons, e.g., aromatics, naphthenes, paraffins, olefins, naphthene-aromatics, etc. using different zeolitic catalysts at different operation conditions [17–22]. Despite the wide variety of hydrocarbons which has been studied at operation conditions reasonably close to those used in industrial cracking, there is a general consensus that a limited number of families of elementary reactions are commonly present in the process of coke formation [23–25].

For instance, the cracking of small olefins and paraffins has been reported to result in the formation of larger products than the reactant [20,21]. The formation of oligomers via alkylation and the presence of a certain amount of aromatics produced via a complex reaction pathway is well documented [7,8,26]. It is clear that the structure of those species is much more complicated than that of the reactant. In addition, the formation of those products has been linked to the presence of carbonaceous deposits on the catalyst.

Derouane et al. [27] proposed a general reaction scheme for coke formation starting from acyclic species where oligomers and aromatics are intermediate species:

$$\text{alkanes} \rightarrow \text{alkenes} \rightarrow \text{oligomers} \rightarrow \text{cycloparaffins} \rightarrow \text{aromatics} \rightarrow \text{coke}$$

A refined scheme was presented by Guisnet and Magnoux [8], who proposed the formation of coke in terms of polyaromatic compounds:

$$\text{alkanes} \rightarrow \text{alkenes} \rightarrow \text{oligomers} \rightarrow \text{cycloparaffins} \rightarrow \text{monoaromatics} \rightarrow \text{polyaromatics}$$

Coke formation, to a higher or lower extent, has been invariantly observed during the catalytic cracking of model hydrocarbons; despite their typically low carbon number compared to the hydrocarbons present a realistic feedstock. It has also been found that the process of coke formation affects the final product distribution due to the interaction of some intermediates participating in this process with other species [20].

Accounting for the deactivation effect of coke on the catalyst activity requires the calculation of the coke content on the catalyst by means of kinetic expressions. Assuming that the different elementary steps require acid sites with different strength, coke formation will have a different deactivation effect on each type of elementary steps [21,28]. Because coke deactivation effects are reaction family dependent, the effects of coke formation on the catalyst performance have to be accounted for using fundamental kinetics. These kinetics are occurring simultaneously and, hence, are interacting with the main catalytic cracking reactions.

The extension of the SEMK methodology to account for coke formation starts with the selection of appropriate species which can be considered as coke precursors [23]. The latter are defined as species which lead via an irreversible step to coke, alkylation being an example. These species are assumed to contribute directly to coke formation via a relatively simple reaction pathway. The formation of the selected coke precursors is to be described in terms of the same elementary reactions as those encountered during the main cracking. This is innovative in the sense that the competition between the coking and cracking and, hence, the effect of coking on the product distribution is, at least partially, inherently accounted for in the kinetics. That complements the traditionally used deactivation functions which, in this methodology, exclusively account for the decrease in available acid sites due to acid site poisoning and to pore blockage by coke [29].

The order of reactivity towards coke of the different types of hydrocarbons depends on their structure: polyaromatics > aromatics > olefins > branched alkanes > normal alkanes. It has been reported that polyaromatic species contained in real feedstocks may contribute directly to coke formation [30]. Their basic character has been correlated to the coking rate. Since polyaromatic species are difficult to be desorbed, they are available for reaction with other species resulting in fast coke formation. Aromatics with three rings whose basic structures are phenantrenic and anthracenic were selected as coke precursors in this work. Those are hydrocarbon structures which can be well represented in the existing reaction network and that move rather slowly through the zeolite pores because of their molecular dimensions [19]. For instance, the pore entry of the Y-zeolite supercage is about 0.75 nm and phenantrene molecule is 0.65 nm × 0.85 nm [8].

2.1. Reaction network refinements leading to coke precursors description

The application of the SEMK methodology for catalytic cracking requires the construction of a detailed reaction network for a chosen hydrocarbon or group of hydrocarbons, on molecular level. Accounting for the rules of the carbenium ion chemistry associated to the various elementary steps, all possible reaction pathways, along with the molecular species and carbenium ions are considered. Due to the large number of species involved the network generation is performed by a computerized algorithm. The vector representation of the species, i.e., their label, is transformed into a Boolean matrix in order to implement the corresponding elementary steps. Afterwards, the product Boolean matrix is reconverted into the corresponding label. This algorithm has been extensively described in the literature [13,16].

To incorporate the formation of coke precursors into the algorithm for the reaction network generation, the appropriate reaction families were included into the code for any type of molecule, e.g., paraffinic, olefinic, naphthenic, aromatic, etc., to be capable of producing the coke precursors. The reaction network must be capable of describing coke precursors starting even from very simple species such as small olefins or paraffins. Forming the defined coke precursors from those types of species is possible by means of a quite complex reaction pathway because of the number of elementary steps and intermediate species which are in between. Nevertheless, once the reaction network can be constructed for very simple acyclic species, the formation of coke precursors from (a) cyclic species with more complicated structures can be automatically constructed.

A detailed reaction pathway for coke precursor formation from 1-butene is illustrated in Fig. 1. A well identified number of elementary steps, also present in the main cracking routes of hydrocarbons, can be identified. The first stage describes the formation of the first cyclic species which is one of the critical steps leading towards coke. This occurs via cyclization of long enough (C_6+) olefinic carbenium ions formed via hydride transfer and isomerization of gas phase olefins. The hydride transfer of olefins produces only allylic carbenium ions. Further on hydride-shifts occur for positioning the charge in gamma or delta positions with respect to the double bond. The existence of

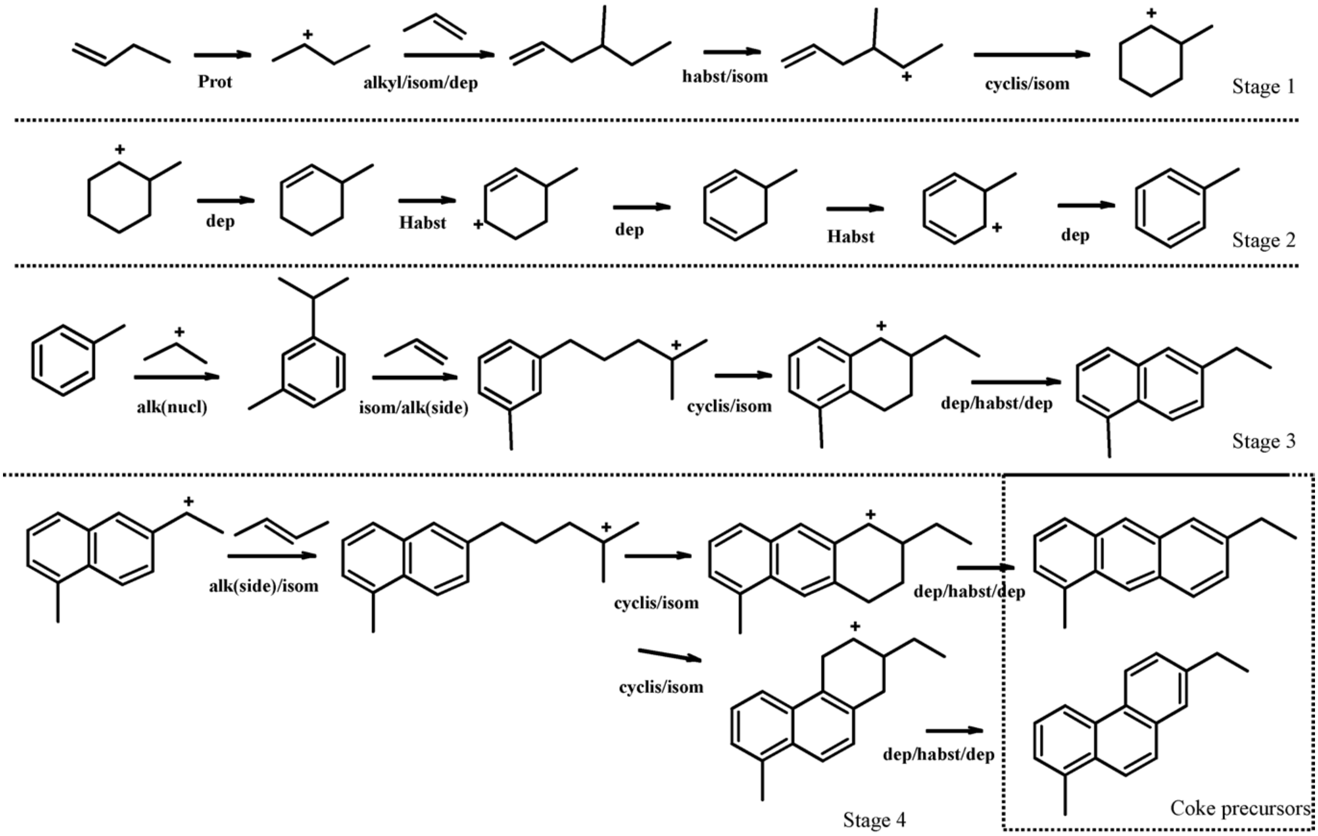

Fig. 1. Detailed reaction pathway for the formation of coke precursors starting from 1-butene. The different stages in the pathway are shown. In order not to overload the figure, the reverse reaction steps have been omitted.

this type of carbenium ions as well as its susceptibility of undergoing self-alkylation has already been considered [23,31,32]. Small acyclic carbenium ions formed via protonation of 1-butene require an alkylation with a gas phase olefin for formation of a species large enough to be able to undergo ring closure reactions.

When the first cyclic molecule has been formed, the selected coke precursors may be produced by different pathways, where the formation of intermediate (poly)aromatics and/or (poly)naphthenes can occur. The formation of completely aromatized species is favored taken into account that the aromatization of cyclic species, involving hydride transfer steps, is faster in comparison to the alkylation/cyclization steps required for the formation of (poly)-naphthenic rings [20].

In the second stage illustrated in Fig. 1, the saturated cyclic molecule undergoes a series of deprotonations and hydride transfer reactions to produce the corresponding aromatic molecule. Both cyclic olefins and cyclic diolefins are formed as intermediates. The aromatic component formed is susceptible to alkylation reactions on the side chain, with small gas phase olefins, and/or on the nucleus, with carbenium ions resulting from the protonation of the same olefins. Subsequent cyclization of the alkyl side chain leads to a naphteno-aromatic component. An additional series of deprotonations and hydride transfer reactions leads to the corresponding diaromatic component as illustrated in Fig. 1 stage 3. The formation of intermediate diaromatic cyclic olefins is accounted for. Finally, the same steps are involved in the formation of triaromatic components which are considered as the coke precursors. It has been assumed that small olefins preferentially participate as alkylant agents because of their high mobility and stability to cracking reactions.

During the whole process for describing coke precursors, the degree of insaturation in the (poly)(aromatic)cyclic molecules gradually increases due to the combination of hydride transfer and deprotonation reactions. The intermediate species formed are susceptible to react with any other species of the network, mainly via hydride transfer. Additionally the supplementary elementary steps considered in the description of the coke precursors formation such as cyclization and alkylation, permit to establish a link between acyclic and cyclic species and to account for different reaction routes species which were not considered in the past [13,14,16].

The described reaction network leading to coke precursors was fully implemented in the computer code and successfully generated starting from relatively simple but representative compounds contained in a real catalytic cracking feedstock, e.g., paraffins (*n*-dodecane), naphthenes (butylcycohexane) and aromatics (hexylbenzene). The constructed reaction network for the cracking of *n*-dodecane contained 1609 cyclizations of olefins, 204 (poly)aromatics side chain alkylations, 3012 (poly)aromatics nucleus alkylations and the formation of 2576 different coke precursors. These have anthracenic and phenanthrenic structures as shown in Fig. 1.

3. Coke formation out of coke precursors: reaction pathways and rate equations

It is well known that polyaromatic components and olefins have strong tendencies to produce coke in catalytic cracking [7,33]. The critical step for coke formation is involving these molecules and, hence, coke formation is increased by their presence in the feedstock next to their formation along the pathway described in the previous section.

The basic character of the polyaromatic species has been correlated to the rate of coke formation whereas the high mobility and the inertia for cracking of small olefins permit an easy interaction with strongly adsorbed species on acid catalysts. Concerning polyaromatic species, one of the critical requirements for coke formation is the presence of long enough side chains on the ring which can undergo further cyclization and subsequently hydride transfer reactions (and deprotonations) leading to additional aromatic rings [7].

As discussed previously, the extended reaction network considers alkylation as an elementary step responsible for the formation of longer side chains in aromatic species, where olefins also play an important role. These alkylation reactions were also considered and implemented in the reaction network to occur on the coke precursors to produce heavier species which can produce coke very rapidly according to the following rules:

- Alkylation of the side chain of coke precursors with small olefins. In first instance, coke precursors undergo hydride abstraction producing the corresponding carbenium ions which next are alkylated with olefins. Ultimately, the alkylated species are transformed potentially very rapidly into coke (Fig. 2).
- Alkylation of the nucleus part of the coke precursors with small carbenium ions formed out of the same olefins. As it was already the case in the nucleus alkylation of mono and diaromatics, carbenium ions produced via protonation of small olefins are considered in the alkylation of coke precursors. A coke precursor is directly alkylated with those carbenium ions producing a species will produce coke potentially rapidly (Fig. 3).

The structure of the alkylated species formed from both alkylations is known and kept track of during the network generation. Nevertheless, those species cannot participate in further reactions in the network because it is assumed they are potentially rapidly transformed into coke.

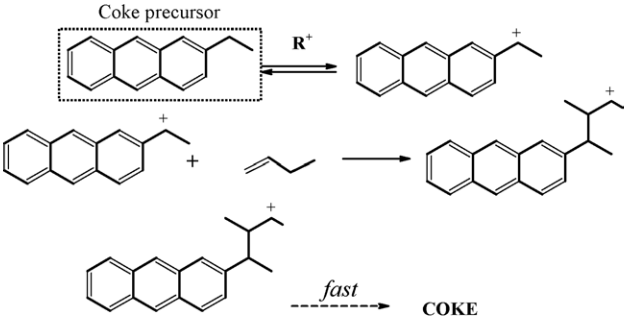

Fig. 2. Reaction pathway of coke formation via side chain alkylation of formed coke precursors. R^+ is any carbenium ion that can abstract a hydride from a coke precursor.

In principle, all olefins are possible reactants for alkylation reactions. In the network generation as discussed here only 'small' olefins, i.e., not susceptible for further cracking, are considered as possible reactants for alkylation because these 'small' olefins are much more stable than 'heavier' olefins which are susceptible to cracking. The 2576 coke precursors formed during the cracking of *n*-dodecane undergo 2498 and 78 nucleus and side chain alkylations, respectively: 2576 species considered as coke are formed.

3.1. Rate equations for coke formation out of coke precursors

The reaction network considers all the possible reaction pathways for the cracking of individual components. For instance, the reaction network for the cracking of *n*-dodecane consists of 37,419 different hydrocarbons and 17,171 different carbenium ions. Considering that the number of species grows exponentially with the carbon atom number, that the current analytical techniques are not capable to give a detailed composition of complex feedstocks and the formed products and that the solution of the continuity equations for all the components in a reaction mixture would lead to excessive calculation times, a certain degree of lumping is required [16].

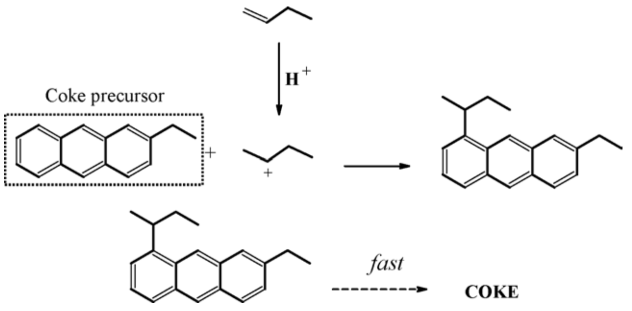

Fig. 3. Reaction pathway of coke formation via alkylation of the nucleus part of formed coke precursors.

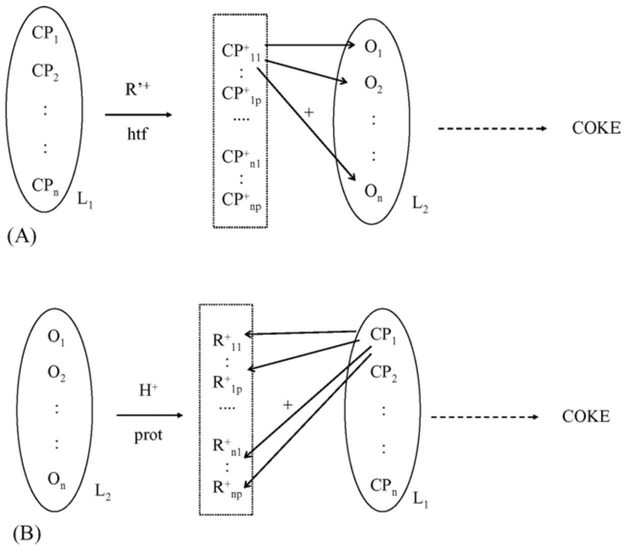

Fig. 4. Lumping scheme of the alkylation reactions of coke precursors leading to coke: (A) side chain alkylation and (B) nucleus alkylation. CP_i are coke precursors, CP^+_{ij} are carbenium ions formed via hydride transfer of coke precursors, O_i are olefins, R_{ij}^+ are carbenium ions formed via protonation of olefins and R'^+ is any carbenium.

The improvements achieved in the reaction network leading to coke permit to propose rate equations in the relumped form. The fundamental character of SEMK is preserved in the relumped form because all elementary reactions occurring between the species of the lumps are accounted for via the so-called lumping coefficient. As a result, this method is denoted as late lumping or relumping [13,16]. The reaction rate between lumps is found by the summation of all elementary reaction steps which transform carbenium ions formed out of the reactant lump into carbenium ions which desorb as molecules of the product lump. The lump definition is based on analytical capabilities. In the relumped SEMK, a distinction is made between paraffins, isoparaffins, olefins, isoolefins, mono, di, tri and tetra-naphthenes (cyclic olefins), mono, di, tri and tetra-aromatics (aromatic olefins), naphthen-mono, di and tri-aromatics per carbon number.

Fig. 4A illustrates the relumping methodology applied to the alkylation reactions for the coke formation from the coke precursors. For instance, Fig. 4A shows that every coke precursor from lump L_1 undergoes hydride abstraction to produce all corresponding carbenium ions. Those are alkylated with the olefins contained in lump L_2. Evidently, each carbenium ion formed from coke precursors can react with each olefin in lump L_2. The rate of consumption of the coke precursors contained in lump L_1 corresponds to the summation of the rates of consumption of the species contained in that lump. To account for this summation the so-called lumping coefficients were defined [13]. These depend only on the generated reaction network and are independent of the single-event rate coefficients.

The rate equation for coke formation via alkylation of the side chain of the components belonging to the lump containing the coke precursors (triaromatics) denoted as L_1, with the olefins of lump L_2, can be expressed by:

$$r^{\mathrm{o}}_{\mathrm{C(alk\_side)}} = P_{L_1}P_{L_2}\theta^+_{\mathrm{B}}\mathrm{MW_C}\sum_{m,n} \times \frac{\tilde{k}_{\beta}(m,n)\tilde{k}_{\mathrm{htr}}(m)LC_{\mathrm{alk\_side\_CP}}(m,n)}{(n_{\mathrm{e}})_{\mathrm{av,dep}}\tilde{k}_{\mathrm{dep}}(m)+\tilde{k}_{\mathrm{htf}}(s)\sum_j (n_{\mathrm{e}})_{\mathrm{htf}}P_{Lj} + \tilde{k}_{\mathrm{htf}}(t)\sum_j (n_{\mathrm{e}})_{\mathrm{htf}}P_{Lj}} \tag{3}$$

$\tilde{k}_{\mathrm{htf}}(m)$ and $\tilde{k}_{\mathrm{dep}}(m)$ are the single-event rate coefficients of hydride transfer and deprotonation respectively involved in the formation and consumption of carbenium ions (m: secondary or tertiary) out of the coke precursors; $\tilde{k}_{\beta}(m,n)$ are the single-event rate coefficients of beta-scission which are used instead of the alkylation ones by applying the reversibility concept, cf. infra. $\mathrm{MW_C}$ is the average molecular mass of coke. The latter is to be estimated by regression of experimental data. Finally, θ^+_{B} is the fraction of acid sites occupied by carbenium ions susceptible of undergoing hydride transfer. The latter is calculated from the quasi-steady state approximation applied to the carbenium ions. P_{L_1} and P_{L_2} are the partial pressures of the lumps participating in the reaction and P_{L_j} is the partial pressure of the lumps of species in the gas phase which are susceptible to hydride transfer. $\mathrm{LC_{alk\_side\_CP}}(m, n)$ is the lumping coefficient which depends only on the reaction network and on the defined lumps:

$$\mathrm{LC_{alk\_side}}(m,n) = \sum_{m,n}(n_{\mathrm{e}})_{\mathrm{alk\_side}}(n_{\mathrm{e}})_{\mathrm{htf}}y_{i,L_1}y_{j,L_2}K_{(\mathrm{CP}_i+\mathrm{O}_j\leftrightarrow \mathrm{CP\_alk}_{ij})} \tag{4}$$

This lumping coefficient can be calculated a priori provided that y_{i,L_1} and y_{i,L_2}, the mole fractions of the species i and j in the lumps L_1 and L_2 are known. An equimolar composition of the lumps is assumed. $(n_{\mathrm{e}})_{\mathrm{htf}}$ and $(n_{\mathrm{e}})_{\mathrm{alk}}$ are the number of single events for hydride transfer and for alkylation reactions.

Analogously, the formation of initial coke via alkylation on the nucleus of the hydrocarbons belonging to the lump L_1 containing the coke precursors with the olefins belonging to lump L_2 can be calculated by the following expression:

$$r^{\mathrm{o}}_{\mathrm{C(alk\_nucl)}} = P_{L_1}P_{L_2}(1-\theta^+_{\mathrm{B}})\mathrm{MW_C}\sum_{m} \times \frac{\tilde{k}_{\mathrm{dealk}}(m)\tilde{k}_{\mathrm{prot}}(m)\mathrm{LC_{alk\_ring\_CP}}(m)}{(n_{\mathrm{e}})_{\mathrm{av,dep}}\tilde{k}_{\mathrm{dep}}(m)+\tilde{k}_{\mathrm{htr}}(s)\sum_j (n_{\mathrm{e}})_{\mathrm{htf}}P_{Lj} + \tilde{k}_{\mathrm{htf}}(t)\sum_j (n_{\mathrm{e}})_{\mathrm{htf}}P_{Lj}} \tag{5}$$

$k_{\mathrm{prot}}(m)$ is the protonation coefficient, $1-\theta^+_{\mathrm{B}}$ is the fraction of free acid sites, i.e., available for the protonation of olefins. The lumping coefficient is calculated from:

$$\mathrm{LC_{alk\_ring\_CP}}(m) = \sum_{m}(n_{\mathrm{e}})_{\mathrm{alk\_nucl}}(n_{\mathrm{e}})_{\mathrm{prot}}y_{i,L_1}y_{j,L_2} \times K_{(O_{\mathrm{ref}}\leftrightarrow O_j)}K_{(\mathrm{CP}_i+\mathrm{O}_j\leftrightarrow \mathrm{CP\_alk}_{ij})} \tag{6}$$

$\tilde{k}_{\mathrm{dealk}}(m)$ is the single-event kinetic parameter for dealkylation which is used instead of the single-event rate coefficient for nucleus alkylation through the reversibility concept.

The reversibility concept was applied to reduce the number of kinetic parameters in the model for coke formation. More precisely, the side chain alkylation of coke precursors is the reverse reaction of an (exocyclic)beta-scission of a triaromatic carbenium ion, and the alkylation of the nucleus part of coke precursors corresponds to the reverse reaction of the dealkylation of triaromatic species [16,34]. Using a group contribution method [35], the beta-scission-side alkylation and dealkylation-nucleus alkylation equilibrium coefficients can be calculated based on the knowledge of the structure of the species involved and, hence, these coefficients are included in the corresponding lumping coefficients, e.g., $K_{(\mathrm{CP}_i+\mathrm{O}_j \leftrightarrow \mathrm{CP\_alk}_{ij})}$ in Eqs. (4) and (6). In this way, the only parameter in the coking rate equations which does not correspond to the main cracking rate equation is the average molecular mass of coke.

Eqs. (3) and (5) express the rate of coke formation via alkylation of a lump of coke precursors with a given number of carbon atoms. As shown in Figs. 1–3, coke precursors have either anthracenic or phenantrenic structures. According to the reaction network, coke precursors can have from 14 to 17 carbon atoms, and, hence, only methyl, ethyl or propyl side chains can be present. Because many coke precursors are formed in the reaction network and because these precursors are lumped according to the carbon number the total rate of coke formation ($r_{\mathrm{C}}^{\mathrm{o}}$) is given by:

$$r_{\mathrm{C}}^{\mathrm{o}} = \sum_{j=1}^{4} r_{\mathrm{C(alk\_side\_CP)}}^{\mathrm{o}} + \sum_{j=1}^{4} r_{\mathrm{C(alk\_nucl\_CP)}}^{\mathrm{o}} \qquad (7)$$

4. Application of the SEMK model for coke formation in a riser-reactor simulator

A simulation of an industrial riser-reactor was performed based on a one-dimensional pseudo-homogeneous model [14]. The most important assumptions and simplifications in the model are listed below:

- instantaneous vaporization of the feedstock at the bottom of the riser: the thermal equilibrium between feedstock and catalyst is achieved;
- catalyst and gas phases move in ideal plug flow with a constant slip velocity;
- adiabatic reactor operation.

The number of lumps considered in the code amounts to 678 including coke as a single lump. Hydrocarbon feedstocks up to C_{40} are dealt with, but the extension to even higher carbon numbers is possible. The feedstock used in the simulation is a partially hydrogenated vacuum gas oil containing globally 26.4 wt% paraffins, 55.8 wt% naphthenes and 17.8 wt% aromatics. Feedstock composition must be given in terms of the described lumps. A detailed characterization has been previously reported [36]. A set of 680 ordinary differential equations consisting of the continuity equations for each lump and the energy equations, has to be integrated as presented below:

For each lump of hydrocarbons:

$$\frac{\mathrm{d}w_i}{\mathrm{d}z} = \frac{\Omega_{\mathrm{r}}\rho_{\mathrm{cat}}(1-\varepsilon)r_i}{F_{\mathrm{g}}^{\mathrm{o}}}, \quad \text{at } z=0;\ w_i=(w_i)_{\mathrm{inlet}} \qquad (8)$$

For coke:

$$\frac{\mathrm{d}C_{\mathrm{C}}}{\mathrm{d}z} = \frac{\Omega_{\mathrm{r}}\rho_{\mathrm{cat}}(1-\varepsilon)r_{\mathrm{C}}}{F_{\mathrm{g}}^{\mathrm{o}}}, \quad \text{at } z=0;\ C_{\mathrm{C}}=(C_{\mathrm{C}})_{\mathrm{inlet}} \qquad (9)$$

For the residence time:

$$\frac{\mathrm{d}\theta}{\mathrm{d}z} = \frac{3600\Omega_{\mathrm{r}}\rho_{\mathrm{cat}}\varepsilon}{F_{\mathrm{g}}^{\mathrm{o}}}, \quad \text{at } z=0;\ \theta=0 \qquad (10)$$

The temperature profile along the riser is calculated form an enthalpy balance. Continuity equations were integrated using a fourth order Runge–Kutta method. Riser-reactor dimensions and operation conditions used in the simulations are presented in Table 1.

The description of the single-event kinetic parameters used in our simulations and their corresponding values calculated at 803 K, are presented in Table 2. These rate coefficients were estimated under coke free conditions from the cracking of pure paraffins, naphthenes and aromatics with relatively simple structure on a commercial catalyst [14]. Hence, an average molecular mass of coke had to be assumed.

The developed SEMK rate equations for coke formation were incorporated in the simulator code. Simulated reaction product yields and coke yield profiles along the riser were obtained. Product yields are defined as kg of product formed/100 kg of feedstock. In addition, a semi-empirical model for coke formation which accounts for the different deactivation extent of the various elementary reactions families [11] was implemented in the code.

Table 1
Riser-reactor characteristics and operating conditions used during simulations of the cracking of partially hydrogenated VGO

Parameter	Value
Riser height (m)	50
Riser diameter (m)	1.2
Feedstock mass flow rate (kg s^{-1})	60.8
Cat-to-oil ratio ($\mathrm{kg_{cat}\ kg_{feedstock}}^{-1}$)	6.0
Feedstock inlet temperature (K)	618
Regenerated catalyst temperature (K)	1003
Catalyst density (kg m^{-3})	1300
Catalyst specific heat (J (kg K)$^{-1}$)	1003
Catalyst particle diameter (m)	8×10^{-5}

Table 2
Single-event rate coefficients used during the simulations: definition and values calculated at 803 K

Single-event rate			
Coefficient	Value[a]	Coefficient	Value[a]
k_{htf}	2.67×10^{-7}	$k_{\mathrm{pro\_c}}(s)$	2.07×10^{-2}
$k_{\mathrm{pr}}(s)$	9.43×10^{-4}	$k_{\mathrm{pro\_c}}(t)$	9.37×10^{-2}
$k_{\mathrm{pr}}(t)$	1.62×10^{-2}	$k_{\mathrm{dep\_c}}(s)^*$	1.50×10^{0}
$k_{\mathrm{dep}}(p)^*$	1.21×10^{-1}	$k_{\mathrm{dep\_c}}(t)^*$	3.49×10^{0}
$k_{\mathrm{dep}}(s)^*$	1.95×10^{-2}	$k_{\mathrm{end\beta}}(s,s)^*$	2.93×10^{-2}
$k_{\mathrm{dep}}(t)^*$	7.78×10^{-3}	$k_{\mathrm{end\beta}}(s,t)^*$	5.25×10^{-2}
$k_{\mathrm{pcp}}(s,s)^*$	4.42×10^{-4}	$k_{\mathrm{end\beta}}(t,s)^*$	2.73×10^{-4}
$k_{\beta}(s,s)^*$	4.98×10^{-2}	$k_{\mathrm{end\beta}}(t,t)^*$	2.38×10^{-3}
$k_{\beta}(s,t)^*$	1.69×10^{-1}	$k_{\mathrm{endprotol}}(p)$	9.52×10^{-7}
$k_{\beta}(t,s)^*$	2.77×10^{-2}	$k_{\mathrm{endprotol}}(s)$	1.04×10^{-7}
$k_{\beta}(t,t)^*$	1.21×10^{-2}	$k_{\mathrm{endprotol}}(t)$	5.30×10^{-6}
$k_{\mathrm{protol}}(p)$	2.92×10^{-7}	$k_{\mathrm{dealk}}(s)^*$	2.24×10^{-2}
$k_{\mathrm{protol}}(s)$	3.73×10^{-7}	$k_{\mathrm{dealk}}(p)^*$	1.19×10^{-1}
$k_{\mathrm{protol}}(t)$	5.37×10^{-6}	k_{cyc}^*	1.04×10^{-3}
$k_{\mathrm{htf\_c}}$	7.34×10^{-7}	k_{disp}^*	3.89×10^{-4}

[a] Units for the parameters marked with (*) are in kmol $(\mathrm{kg_{cat}\ s\ K})^{-1}$. For the others units are in kmol $(\mathrm{kg_{cat}\ s\ K\ kPa})^{-1}$.

4.1. Semi-empirical rate equation for coke formation

This equation considers only an intermediate degree of detail for coke formation. The coke formation does not interact directly with the main cracking routes. Consequently, the coke effects are accounted for by deactivation functions only [11]:

$$r = r_{\mathrm{C}}^{\mathrm{o}} \Phi \tag{11}$$

Two consecutive reactions are involved in coke formation: primary coke formation and coke growth [11,37]. Since the various elementary reactions occurring simultaneously during catalytic cracking have different activation energies and require different minimum acid site strength to proceed, the deactivation effects depend on the type of elementary reaction and, hence, more than one deactivation function (Φ_k) must be used [15,20]. The semi-empirical model used for coke formation considers several deactivation functions which depend on the primary coke content (C_{s}) as well as the corresponding deactivation constant (α_k) [11]:

$$\Phi_k(C_{\mathrm{s}}) = \exp(-\alpha_k C_{\mathrm{s}}) \tag{12}$$

At the investigated conditions more than 99 % of the total coke content consisted of primary coke. Primary coke is proportional to the amount of deactivated sites. The deactivation effect of coke on the different types of elementary reaction families as a function of coke content on the catalyst is presented in Fig. 5. Hydride transfer, protolytic scission and beta scission are the most susceptible to deactivation. That is reasonable since hydride transfer is a bimolecular reaction requiring high acid sites density and protolytic cracking occurs on strong acid sites. On the other hand, deprotonation and pcp-isomerization are deactivated to a very low extent. The coke formation rate is more strongly deactivated than any other elementary reaction family (Fig. 5B). The coke content on the catalyst at the riser outlet amounts to 0.29 wt%.

4.2. SEMK rate equation for coke formation

In the developed SEMK rate equation for coke formation, the process of coking is fully linked to the main cracking process in the sense that intermediate species leading to coke precursors can interact with, i.e., compete and/or inhibit, the cracking reactions. As a result, in principle no empirical

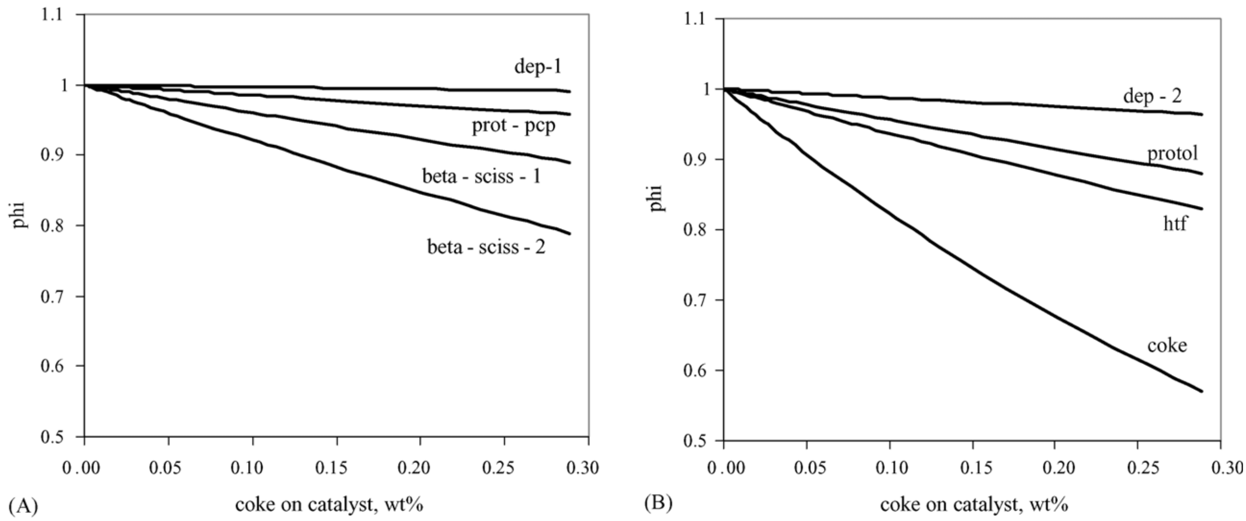

Fig. 5. Deactivation functions of different elementary reaction families vs. catalyst coke content: beta sciss-1 corresponds to (*s*,*s*), (*t*,*s*) and (*t*,*s*) and beta sciss-2 to (*t*,*t*); dep-1 is for (*p*) and (*s*) and dep-2 for (*t*); protol, htf and prot-pcp corresponds to protolytic scission, hydride-transfer and protonation-pcp isomerization, respectively. *p*, *s* and *t* are primary, secondary and tertiary carbenium ions. Information obtained during the cracking of partially hydrogenated VGO with the semi-empirical coke model [2]. Operation conditions according to Table 1.

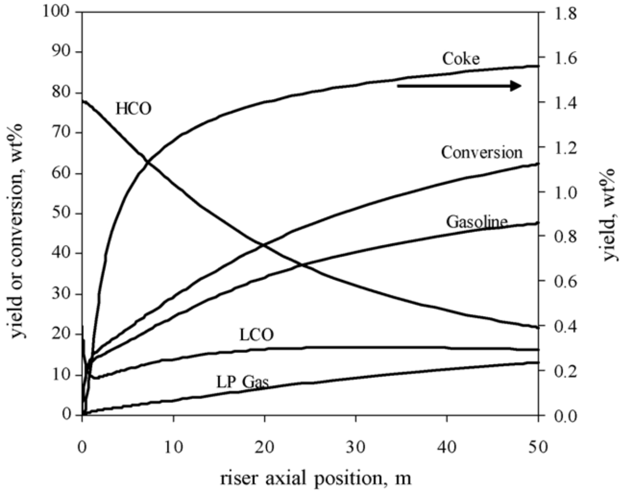

Fig. 6. Product yields (LP Gas, gasoline, LCO, HCO and coke) and conversion versus axial riser coordinate. Information obtained with the SEMK model for coke formation during the cracking of a partially hydrogenated VGO. Operation conditions according to Table 1.

deactivation functions have to be used and no pore blockage occurs. Nevertheless, these functions might be required to account for the effect of the acid site strength distribution on the deactivation of the various families of elementary reactions. The average molecular mass of coke was assumed to be 250 g mol^{-1}, which correspond to the molecular mass of a polyaromatic species with five to six rings that are practically trapped in the zeolite pores. Fig. 6 shows the axial profiles, under the operating conditions used in the simulation (see Table 1), of the typical product yields reported in a refinery, i.e., LP Gas: C_3–C_4, gasoline: C_5–C_{12}, light cycle oil (LCO): C_{13}–C_{20} and heavy cycle oil (HCO): C_{21}–C_{40}, and conversion defined as:

$$100 - \text{HCO wt\% yield} - \text{LCO wt\% yield} \qquad (13)$$

The presented reaction product profiles are in a good agreement to those reported elsewhere [38,39]. Namely, it is evident that during the first meters of the riser, where the regenerated hot catalyst contacts the fresh feedstock containing the most reactant hydrocarbons, an important fraction of the feedstock is converted mainly to gasoline. The cracking of long paraffins and long side chains encountered in (poly)naphthenes and poly(aromatics) contributes importantly to gasoline formation when the reaction starts, then a slower increase in gasoline production is observed from 30 m onwards which reflects that gasoline precursors of the feedstock have been practically consumed. The reaction severity at which the simulations were performed (cat-to-oil ratio = 6.0) did not lead to a global gasoline overcracking. On the other hand, the LP Gas yield that is produced via both primary (from feedstock) and secondary (from LCO and gasoline) cracking always increases as a function of the riser position. At the riser top more than 60 wt% of the feedstock was converted whereas gasoline and LP Gas yield reached 47 and 13 wt% respectively. These values are reasonable compared to industrial data where typical conversions, gasoline and LPG yields are in the order of 70, 45 and 18 wt%, respectively. The product vapours–catalyst mixture temperature was 795 K which is 35 K lower than the mixture temperature at the riser bottom at the operating conditions presented in Table 1. The residence time of the hydrocarbons in the riser was close to 3 s. Typical values are in the range of 2–5 s.

Coke yield profile along the riser obtained using SEMK can also be observed in Fig. 6. Coke formation shows a sharp increase in the first meters of the riser which has been observed in industrial operation and reported in literature [38,39]. The fast coke deposition on the catalyst shown by the SEMK indicates that coke precursors contained in the feedstock are immediately converted to coke. The predicted coke yield by this model at the riser top amounts to 1.5 wt% against 1.7 wt% reported by the semi-empirical model. That corresponds to 0.26 and 0.29 wt% coke content on spent catalyst respectively. Those values are certainly low compared to typical industrial values which vary from 0.5 to 1.2 wt%. One reason for that difference could be that only catalytic coke is accounted for in the simulation and that additionally the properties of the feedstock indicate a moderated tendency of producing coke due to its naphthenic character and a lower concentration of aromatics.

5. Conclusions

A methodology based on Single-Event MicroKinetics (SEMK) was applied to model coke formation in catalytic cracking. Coke was proposed to be formed out of coke precursors with a polyaromatic structure. Their formation is described in terms of a limited number of elementary reactions families, i.e., alkylations, cyclizations, hydride-transfers and (de)protonations requiring no additional kinetic parameters. The actual coke formation occurs via alkylation of the side chain or the nucleus of the coke precursors with relatively small olefins or the corresponding carbenium ions. The average molecular mass of coke is the only parameter to be determined from experimental data.

An industrial riser-reactor was simulated including the SEMK model for coke formation. Simulation profiles related to reaction products and coke yields are in reasonable agreement with typical industrial ones.

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