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Coke formation in fluid catalytic cracking studied with the microriser

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Abstract

The catalysts used in the fluid catalytic cracking process are reversibly deactivated by deposition of coke. The coke deposition and its effect on the activity of the catalyst in the reactor have been studied using the microriser, a laboratory-scale entrained flow reactor. The experimental results show that the timescale of coke formation is much shorter than the timescale for conversion. Coke deposition mainly occurs initially (within 0.15 s), while the conversion increases during the whole residence time in the reactor (0–5 s). A five lump kinetic scheme has been used to model the measurements with a constant catalyst activity and with a catalyst activity that decreased with time on stream. It is shown that the results obtained after 0.15 s can be modeled with a constant activity, so initial coke deposition is the main cause of deactivation. It is proposed that the initial effects, coke deposition accompanied by formation of products, and catalyst deactivation, have to be described with a separate model that takes into account catalyst-to-oil ratio, feedstock, and catalyst properties. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Fluid catalytic cracking; Modeling; Coke; Deactivation; Kinetics; Entrained flow reactor

1. Introduction

Fluid catalytic cracking is an important industrial oil conversion process for the production of gasoline and diesel range hydrocarbons. It also is a major industrial application of a riser or entrained flow reactor. In an entrained flow reactor solids (catalyst particles) are transported by a gas flowing at a high velocity. This reactor type is favorable in catalytic reactions where: (a) the catalyst circulation rate has to be high due to a rapid deactivation; (b) an intermediate product is the desired product (partial oxidations or hydrogenations); (c) a periodic operation is beneficial (regeneration or reactivation of the catalyst is necessary); (d) the reactions are highly exothermic or endothermic [1,2]. All these reasons are more or less valid for the FCC process as will be explained below.

In the FCC process the riser is used for the conversion of hydrocarbons using a very active zeolite based catalyst [3]. During the residence time of the catalyst in the riser reactor (1–10 s) the catalytic activity is strongly diminished by the deposition of coke. After stripping the catalyst to remove adsorbed and entrained hydrocarbons, the catalyst is transported to the regenerator, where the coke is burnt off. The regenerated catalyst is recycled to the riser reactor.

The riser/regenerator system is heat-balanced; the heat necessary for the vaporization of the feedstock and the endothermic cracking reactions is generated in the regenerator by the exothermic combustion of the deposited coke [3,4]. The conversion that can be

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obtained in the process is determined by the coke build-up on the catalyst in the riser. The amount of coke determines the heat that can be generated in the regenerator, and thereby the amount of heat that can be used for the cracking reactions.

The important influence of the coke deposition on the performance of the whole FCC unit makes it necessary that, when modeling the cracking process, an adequate description of the deposition of coke and the deactivation by coke exists. The present paper aims at analyzing the coke deposition mechanism and the associated deactivation kinetics. To this aim, cracking experiments will be described that have been performed using a microriser, a novel laboratory-scale entrained flow reactor. The results obtained will be modeled using a five lump kinetic scheme with a simple activity function. The choice of this activity function shall be based on the observed coke yield as a function of the operating variables residence time (τ) and catalyst-to-oil ratio (CTO).

2. Theory

A commonly used, simplified model to describe FCC cracking kinetics is the five lump model according to Corella and Francés [5], as depicted in Fig. 1. In this model different components are lumped together into pseudo-components according to their boiling point and only the different relevant reactions between these lumps are taken into account. The different lumps, as defined in Table 1, are: heavy cycle oil (HCO), light cycle oil (LCO), gasoline, gas, and coke. The weight fractions of the different lumping groups are represented by y_1–y_5, respectively. For a fundamental description of the cracking kinetics this model is not suitable, since properties of the feedstock and catalyst are not incorporated in the model, and the product quality of the different lumps is not taken into account. The catalyst and feedstock properties affect the values of the reaction rate constants and when using such a simplified kinetic scheme, it is necessary to measure and evaluate the reaction rate constants for every new combination of catalyst and feedstock. Kinetic models based on elementary steps, in principle, do not suffer from these disadvantages [6–8], but the mathematics are more complex and a large number of parameters are necessary to describe the system adequately. The present paper aims at analyzing the coke deposition mechanism and the associated deactivation kinetics. Especially, the objective is to check the observations of possible initial coke deposition and deactivation that will be described in the next part of this paper. For these purposes a relatively simple model as the five lump model will be satisfactory. A simpler model like the three lump model proposed by Weekman [9] is not sufficient since coke is not treated as a separate lump.

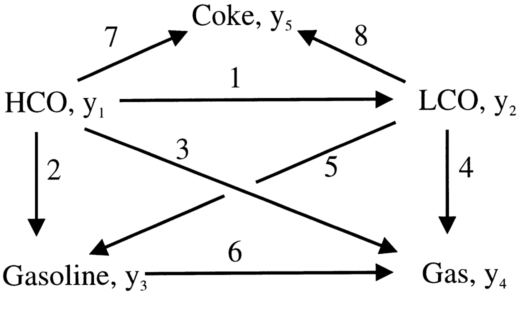

Fig. 1. Reaction scheme of the five lump model [5].

Table 1
Definition of the lumps used in the five lump model according to Corella and Francés [5]

Lump		Composition/boiling point range
Gas	y_4	H_2, C_1–C_4
Gasoline	y_3	C_5, <494 K
LCO	y_2	494–643 K
HCO	y_1	>643 K
Coke	y_5	Carbon deposit

The general equation for the reaction rate of reaction j is given by

$$r_j = \Phi_j k_j y_i^{n_i}, \tag{1}$$

in which r_j is the reaction rate ($\mathrm{kg}_i\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{s}^{-1}$), Φ_j the activity function, a/a_0, k_j the reaction rate constant ($\mathrm{kg}_i^{1-n}\,\mathrm{kg}_{\mathrm{feed}}^{n}\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{s}^{-1}$), y_i the weight fraction of component i ($\mathrm{kg}_i\,\mathrm{kg}_{\mathrm{feed}}^{-1}$), and n_i is the reaction order for component i.

The values used for the reaction order n are 2 for the reaction of HCO, 1.5 for the reaction of LCO, and 1 for the reaction of gasoline [5,10,11]. As a first simplification the activity function will be taken to be the same for all components ($\Phi_j = \Phi$). Using the reaction scheme given in Fig. 1 and the reaction rates as described by Eq. (1), in combination with a plug-flow reactor model, mass balances can be derived for the different lumped groups, resulting in:

$$\frac{\mathrm{d}y_1}{\mathrm{d}\tau} = \Phi\,\mathrm{CTO}(-k_1 - k_2 - k_3 - k_7)y_1^2, \tag{2}$$

$$\frac{\mathrm{d}y_2}{\mathrm{d}\tau} = \Phi\,\mathrm{CTO}(k_1 y_1^2 + (-k_4 - k_5 - k_8)y_2^{1.5}), \tag{3}$$

$$\frac{\mathrm{d}y_3}{\mathrm{d}\tau} = \Phi\,\mathrm{CTO}(k_2 y_1^2 + k_5 y_2^{1.5} - k_6 y_3), \tag{4}$$

$$\frac{\mathrm{d}y_4}{\mathrm{d}\tau} = \Phi\,\mathrm{CTO}(k_3 y_1^2 + k_4 y_2^{1.5} + k_6 y_3), \tag{5}$$

$$\frac{\mathrm{d}y_5}{\mathrm{d}\tau} = \Phi\,\mathrm{CTO}(k_7 y_1^2 + k_8 y_2^{1.5}), \tag{6}$$

in which τ is the residence time based on outlet conditions (s), and CTO is the catalyst-to-oil ratio ($\mathrm{kg_{cat}\,kg_{feed}^{-1}}$).

As a first estimation the activity of the catalyst will be based upon the residence time of the catalyst in the reactor, represented by the following equation:

$$-\frac{\mathrm{d}\Phi}{\mathrm{d}\tau} = k_\mathrm{d}\Phi^m, \tag{7}$$

in which k_d is the deactivation rate constant (s^{-1}), m is the order of deactivation.

In practice, the deactivation is caused by coke and the activity function should have a relationship with the coke deposition. Coke is a general term referring to carbonaceous deposits that can have different origins of formation, different compositions, and different effects on the catalyst activity. Based on discussions in [12–15], the coke deposited in the FCC process can be divided into several types:

1. *Thermal coke*. This is the coke that is deposited on the outer core of the catalyst particle due to thermal degradation of the hydrocarbons of the feedstock when it is contacted with hot catalyst. The amount of thermal coke will be at maximum equal to the so-called Conradson carbon residue (CCR) of the feedstock. This type of coke will cause deactivation mainly due to blocking the access to the catalytic sites inside the catalyst.
2. *Adsorption coke*. This is the coke that results from a strong irreversible adsorption of hydrocarbons onto the catalyst surface. Adsorption coke can be divided into feed adsorption coke and catalyst adsorption coke. Feed adsorption coke is related to feedstock properties such as the aromatics content, the content of highly basic molecules, or the boiling point distribution (incomplete vaporization of the feedstock may result in so-called "soaking coke"). Catalyst adsorption coke is caused by irreversible adsorption of hydrocarbons to strong acidic sites, or by the entrapment of hydrocarbons in cavities and pores of the catalyst. The timescale of formation and deactivation by adsorption coke is relatively short, and may be governed by diffusion resistance.
3. *Catalytic coke*. This is the coke that is deposited on the catalytic sites as a side-product of catalytic cracking due to hydrogen transfer reactions. The timescale of formation is the same as the timescale for conversion. It deactivates the catalyst by the direct coverage of active sites.
4. *Contaminant coke*. This is the coke that is deposited as a result of excessive dehydrogenation reactions catalyzed by contaminants on the catalyst, like nickel. The timescale of formation is expected to be the same as the timescale for conversion, thereby changing the activity and selectivity of the catalyst.

In Fig. 2 generalized trends expected for the coke yield as a function of residence time and of CTO are shown for the types of coke discussed above. When the coke is deposited initially, the activity of the catalyst will not be a function of the residence time. This can be represented by taking the deactivation rate constant k_d in Eq. (7) equal to 0.

3. Experimental

Cracking reactions were performed using the microriser. The microriser is a laboratory-scale entrained flow reactor that can be used as a general testing tool for reactions that occur in the entrained flow regime [16,17]. The reactor can be operated in an ideal plug-flow regime, is isothermal, and the residence time can be varied by changing the reactor length, without changing the catalyst and feedstock flow rates. A schematic drawing of the equipment is given in Fig. 3. The actual reactor consists of a bended tube (bend radius 0.09 m) with an inner diameter of

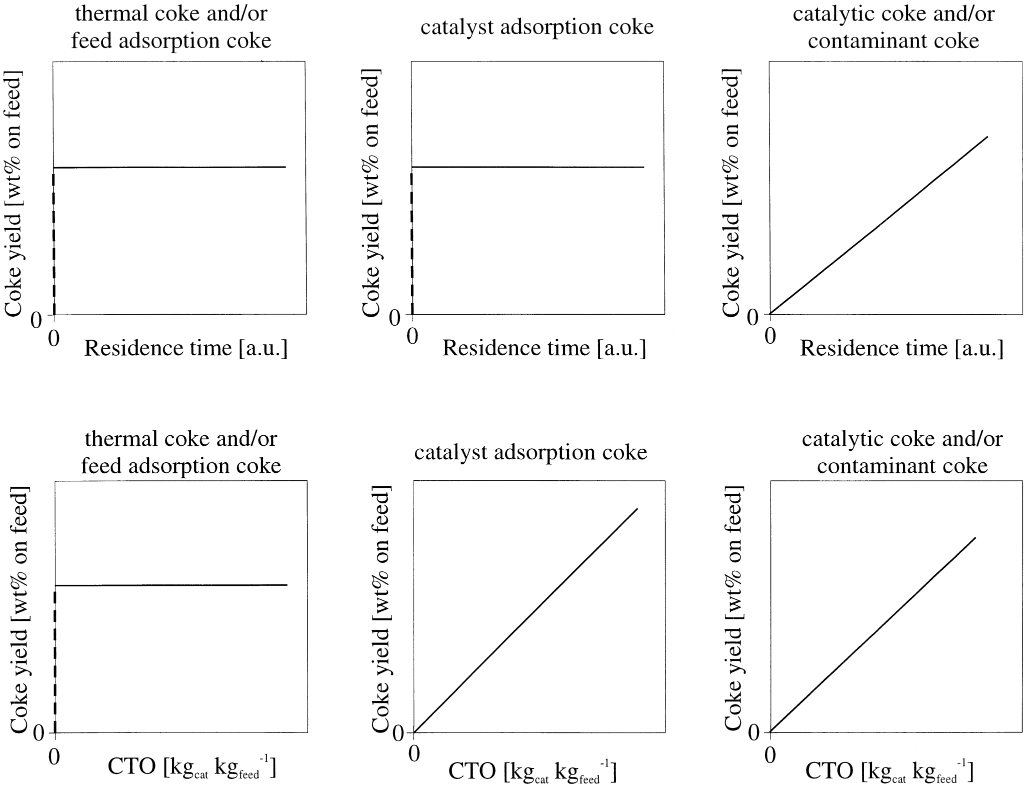

Fig. 2. General trends, expected for coke yield as a function of residence time and CTO for the different coke types (upper part: dependency on residence time, lower part: dependency on CTO). Left: the profiles of thermal coke and feed adsorption coke; center: profiles of catalyst adsorption coke; right: profiles of catalytic coke and contaminant coke.

4.55×10^{-3} m. The length of the reactor can be varied to obtain residence times of the oil and catalyst based on outlet conditions between 0.15 and 5 s. Nitrogen is used as a transport gas for the catalyst. The catalyst is introduced into the gas stream using a catalyst feeding system based on the design given by Horsley and Rothwell [18], in which a rotating wheel continuously removes the catalyst from a hopper. The rotational speed of the wheel determines the catalyst feeding rate. The catalyst is transported to the reactor via a preheat oven. The feedstock is also preheated and injected perpendicular into the down-flowing stream of catalyst and nitrogen. Downstream of the reactor, the catalyst is separated from the gas flow by means of a cyclone and stored in a hopper for post-run stripping. The gas is stepwise condensed and the gaseous products are collected in a Tedlar gas bag. In a typical experiment the products are collected during 20 min of steady-state operation.

Previous work [16] has shown that at a decreasing gas velocity, the degree of mixing of the catalyst in the reactor increases. When the gas velocity is chosen high enough (>4 m s^{-1}) the catalyst flows smoothly through the bends of the reactor in a flow regime that is called the homogeneous flow regime. Residence time distribution measurements have shown that the particle flow can be represented by a combination of a plug-flow reactor (PF) and a continuously stirred tank reactor (CSTR) in series, in which the residence time in the PF is 70 times longer than the residence time in the CSTR. Thus 98.6% of the total residence time of the system correlates with plug-flow behavior.

Within this homogeneous flow regime experiments were performed using a typical FCC equilibrium catalyst and a Hydrowax feedstock. This feedstock is characterized by a low aromatics content, a low CCR and very low sulfur and metal contaminant concentrations. An overview of the feedstock proper-

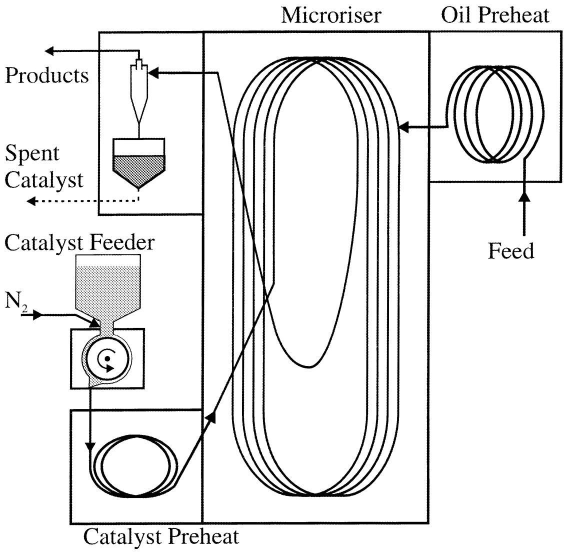

Fig. 3. Schematic representation of the microriser equipment [18].

Table 2
Hydrowax feedstock properties

Density (288 K) (kg m^{-3})	850
Conradson carbon residue (wt%)	0.09
Basic nitrogen (ppm)	12
Sulfur (wt%)	0.01
Vanadium (ppm)	–[a]
Nickel (ppm)	–[a]
Boiling point composition	
Initial boiling point (K)	607
Final boiling point (K)	823
>643 K (wt%)	92.8
>798 K (wt%)	7

[a] Below detection limits (<0.5 ppm wt).

Table 3
Reaction conditions

T (catalyst preheat) (K)	948
T (reactor) (K)	798
T (stripper) (K)	798
p (reactor) (10^5 Pa)	1.1
ϕ_{N_2} (transport) (m^3 s^{-1}) (STP)	1.6×10^{-5}
ϕ_{N_2} (strip) (m^3 s^{-1}) (STP)	8.6×10^{-6}
τ (outlet conditions) (s)	0.15–5
CTO ($kg_{cat}\,kg_{feed}^{-1}$)	0–6

ties can be found in Table 2. At the oil injection point preheated feedstock, at a feeding rate of 0.067 g s^{-1}, was injected perpendicular to the catalyst flow. The CTO was varied between 2 and 6 by adjusting the catalyst feed rate. The reaction conditions used are given in Table 3. To check the amount of thermal cracking, experiments were performed without catalyst. The composition of the gaseous product was determined by gas chromatography, simulated distillation was used to determine the boiling point distribution of the liquid product, and the amount of carbon on the catalyst was determined using a LECO carbon analyzer. A detailed overview of the analytical procedures is given by Helmsing [11]. After each experiment the catalyst was regenerated in an external regenerator. Throughout the whole series of experiments the regenerated catalyst had the same activity and selectivity to the different products.

The results were modeled using the five lump model given above. The parameters of the model, the reaction rate constants k_i and the deactivation constant k_d, were calculated using a Levenberg–Marquardt routine [19].

4. Results

All experiments had mass balances of 98±2 wt%. The conversion and coke yield as a function of residence time at different CTOs are shown in Fig. 4. The coke yield is the part of the feedstock converted to coke, the conversion can be calculated according to

$$\text{conversion} = \frac{y_{1,\text{feedstock}} - y_1}{y_{1,\text{feedstock}}} 100\,\text{wt\%}. \qquad (8)$$

The conversion obtained without catalyst is a measure for the amount of thermal cracking. At a residence time of 4 s the conversion without catalyst is at maximum 6 wt%. In these experiments no coke formation could be observed.

At 0.15 s residence time the conversions measured are already over 30 wt%. At the same time coke yields of 1–1.5 wt% have been found, depending on the CTO. Higher CTOs yield a higher conversion and more coke. The conversion increases proportionally with residence time up to ca. 75 wt%, then levels off and reaches a maximum value of 90–95 wt%. The coke yield is not influenced by residence time at CTOs up to 4. At a CTO of 6 a small increase in coke yield can be found during the first second of the residence

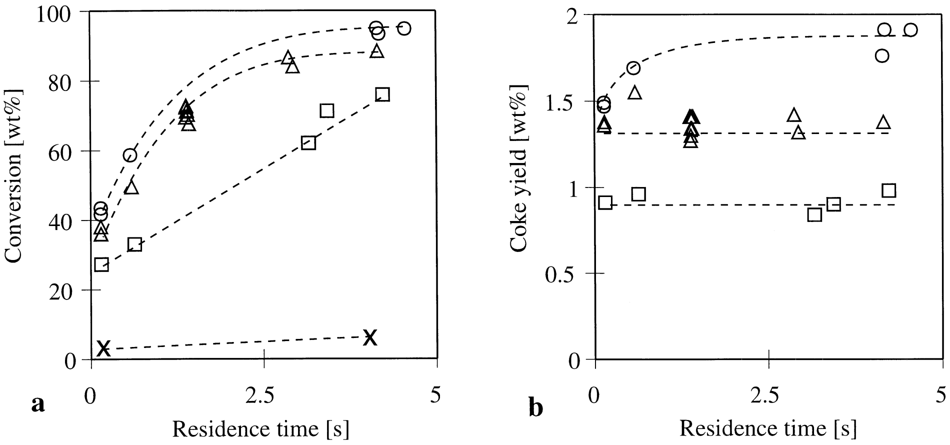

Fig. 4. Conversion (a) and coke yield (b) as a function of residence time at different catalyst-to-oil ratios (CTO): (□) CTO=2, (△) CTO=4, (○) CTO=6, and (×) no catalyst. The dotted lines were drawn to guide the eye.

time. Thus, coke yield is for the major part influenced by the CTO. This is illustrated in Fig. 5, where the coke yield is shown as a function of CTO for all residence times. All measured coke yields can be described according to

$$\text{coke yield (wt\%)} = 0.45 + 0.22 * \text{CTO}. \tag{9}$$

To exclude initial or entrance effects, only the data measured after 0.15 s were used for modeling of the results. To be able to do this, the data measured at 0.15 s were used to define an imaginary feedstock composition, e.g. at different CTOs the composition of the gas stream at 0.15 s was known from the experiments and taken as a starting point for modeling the reactions between 0.15 and 5.0 s. The activity function given by Eq. (7) was used with different deactivation orders; the results for a constant activity (k_d=0) and a first-order deactivation (m=1) are given in Table 4. In this table the calculated values for the parameters of the model, the reaction rate constants k_i, and the deactivation constant k_d are given. The error that is given in this table illustrates the 95% confidence interval of the parameters. It can be seen that the relevant reaction rate constants of the two models, with a value larger than 10^{-2}, are the same. The other

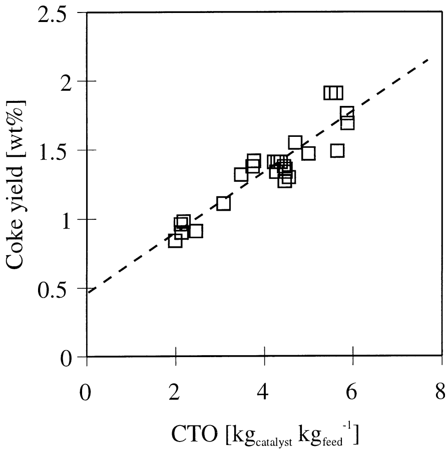

Fig. 5. Coke yield, measured at different residence times, as a function of CTO. The line represents the best linear fit of the measured data.

Table 4
Reaction rate constants and 95% confidence intervals calculated for the data at residence times higher than 0.15 s using a constant activity (k_d=0), and a first-order deactivation (m=1)

	k_d=0	m=1
k_1	0.11±0.03	0.10±0.04
k_2	0.20±0.03	0.20±0.05
k_3	0.037±0.013	0.037±0.054
k_4	≈0	(0.038±170)×10^{-3}
k_5	0.18±0.07	0.18±0.17
k_6	(0.20±0.21)×10^{-2}	(0.20±0.96)×10^{-2}
k_7	(0.18±17)×10^{-3}	≈0
k_8	≈0	≈0
k_9=k_d	–	≈0
SS_{res}	0.60×10^{-3}	0.61×10^{-3}

parameters have either a very low value, or a high inaccuracy, and will not be taken further into consideration. The sum of squares residual (SS_{res}) can be directly compared, since it has been normalized for the number of parameters.

5. Discussion

From Fig. 4 it is clear that the timescale for conversion is much larger than the timescale for coke formation. After a sharp initial increase, the conversion measured at 0.15 s is already over 30 wt%, the conversion increases further with increasing residence time and after 5 s the conversion obtained is 75–95 wt%, depending on the CTO used. In contrast to this, the coke yield is hardly a function of residence time. Except for a CTO of 6, the coke yield found after 0.15 s is the same as the final coke yield. This leads to the conclusion that the major part of the coke is deposited initially. Instead of a function of residence time, the coke yield is a function of CTO, as can be seen from Fig. 4(b) and Fig. 5. If these figures are compared to the generalized coke profiles for the different coke types given in Fig. 2, it can be seen that the coke has to be built up out of different types of coke. The intercept of the curve in Fig. 5 (0.45 wt%) can be caused by thermal coke and/or feed adsorption coke. The CCR of the feedstock is only 0.09 wt%, see Table 2, and the temperature of both feedstock and catalyst at the point of mixing is 798 K, so that the formation of 0.45 wt% thermal coke is not very likely. On the other hand, 7 wt% of the feedstock has a normal boiling point that is higher than this mixing temperature. Although the partial pressure of the hydrocarbons at the reactor entrance is only 20 kPa, the timescale of evaporation shall be very small, in the order of µs. It is possible that, due to improper feed injector design, a small portion of the feedstock is not completely evaporated, resulting in the formation of ''soaking coke''. Another possibility for the *observed* initial coke deposition could be insufficient stripping of the catalyst downstream of the reactor. Test-runs with different stripping times have shown that the used stripping time of 20 min is more than enough to remove all adsorbed hydrocarbons [20]. On an average 0.45 wt% coke can be considered to be deposited initially as a result of incomplete evaporation of the feedstock. During the experiments that have been performed without catalyst no coke deposition (on the hardware) has been observed. Due to the absence of catalyst, ''soaking coke'' should be deposited on the hardware, but it is more likely that the small liquid droplets are entrained with the gas flow, and end up in the liquid product as non-converted feedstock.

The additional coke that is formed as a function of CTO, 0.22∗CTO, has to be catalyst adsorption coke, since this is the only type of coke given in Fig. 2 that is initially formed as a function of CTO.

Significant amounts of catalytic coke or contaminant coke are only observed at a CTO of 6 (compare Fig. 4(b) to Fig. 2), where the coke yield slightly increases as a function of residence time.

The cracking reactions are deactivated by coke deposition. It has been observed that coke deposition is mainly initial. Therefore, the deactivation has to be initial too. This is confirmed by the modeling results (Table 4). In two different ways, these results show that the data were obtained in a constant activity regime. Firstly, the model that uses a constant activity describes the measured data adequately (see also Fig. 6). Secondly, the model that takes deactivation as a function of residence time into account describes the measured data best without deactivation. Therefore, the two used models are identical. The SS_{res} of the two model fits are almost the same; however, since the model without deactivation uses less parameters to describe the measured data, this model can be considered to be the most adequate. In this model, the reaction rate constant k_4, representing the formation of gas from LCO, should also be considered zero, indicating that gas is mainly a primary product directly formed from HCO. Gasoline is mainly a primary product formed from HCO, but also a secondary product via LCO (between 0.15 and 5 s).

The description of the product yields according to the model with a constant activity compared to the experimental data can be found in Fig. 6. From this figure it can be seen that the measured data are accurately described by the model for the whole residence time range. In this figure the composition of the feedstock is also given by the data points at zero residence time. It is clear that between these points and the first measured data at 0.15 s a discontinuity occurs. This is caused by the initial coke deposition and deactivation that shall be accompanied by some con-

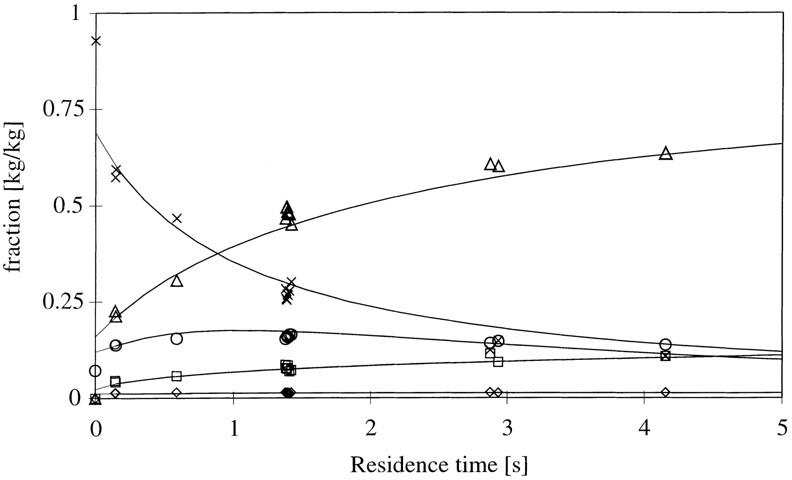

Fig. 6. Comparison of experimental data measured at a rounded CTO of 4 with calculated values using the model developed for the data between 0.15 and 5 s with a constant activity (k_d=0). Symbols: (×) y_1 (HCO), (○) y_2 (LCO), (△) y_3 (gasoline), (□) y_4 (gas), and (◇) y_5 (coke). Symbols refer to measured data, curves are calculated by the model.

version to the other products. The model with a constant activity between 0.15 and 5 s cannot describe the reactions occurring at the entrance of the reactor. These observations support the assumption that the observed initial coke yield is indeed initial and not a result of insufficient stripping.

Overall, the results discussed make it clear that to model the reaction kinetics in the FCC microriser including the initial effects, a different model should be developed that combines the initial effects (coke deposition, deactivation, and conversion to other products) with a constant rest activity of the catalyst.

6. Conclusions

The microriser is a laboratory-scale entrained flow reactor that can be operated in an ideal plug-flow regime when the gas velocity is high enough. The reactor can be used to study the kinetics of catalytic cracking and the coke deposition, even at a very short timescale, since the length of the reactor can be easily varied.

It has been shown that the timescale of coke deposition and thus of deactivation is much smaller than the timescale of conversion. The deposition of coke for the major part takes place initially and is hardly a function of residence time. The coke yield is largely determined by the catalyst-to-oil ratio (CTO). When different coke types are considered, only the formation of adsorption coke is in agreement with the observed effects. Adsorption coke related to the feedstock properties is responsible for approximately 0.45 wt% non-catalytic coke. This is probably for the major part of the result of incomplete vaporization of the feedstock, resulting in small liquid droplets that come partly into contact with the catalyst and are immediately converted to coke, and are partly entrained with the gas flow without further conversion. The rest of the coke that is formed is proportional to the amount of catalyst fed to the reactor and can be considered to be catalyst adsorption coke.

The deactivation caused by coke deposition is for the major part initial, since the data measured after 0.15 s residence time could be modeled with a constant activity.

It is clear, that to model both the initial effects and the conversion in the rest of the reactor, a more complicated activity function has to be used. This activity function should account for an initial deactivation resulting from the coke deposition, and a constant residual activity. Since coke yield is for the major part determined by the CTO and by the catalyst and feedstock properties, this activity function should be a function of CTO, catalyst, and feedstock properties, as well.

7. List of symbols

a	activity of the catalyst $(\mathrm{kg}_i\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{s}^{-1})$
CTO	catalyst-to-oil ratio $(\mathrm{kg}_{\mathrm{cat}}\,\mathrm{kg}_{\mathrm{feed}}^{-1})$
k	reaction rate constant $(\mathrm{kg}_i^{1-n}\,\mathrm{kg}_{\mathrm{feed}}^{n}\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{s}^{-1})$
k_d	deactivation rate constant (s^{-1})
m	order of deactivation (dimensionless)
n	order of the reaction (dimensionless)
p	pressure (Pa)
r	reaction rate $(\mathrm{kg}_i\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{s}^{-1})$
$\mathrm{SS}_{\mathrm{res}}$	normalized sum of squares residual (dimensionless)
T	temperature (K)
y	weight fraction $(\mathrm{kg}\,\mathrm{kg}_{\mathrm{feed}}^{-1})$

Greek symbols

Φ	activity function, a/a_0 (dimensionless)
ϕ	volumetric flow, STP $(\mathrm{m}^3\,\mathrm{s}^{-1})$
τ	residence time based on outlet conditions (s)

Subscripts

0	at time zero
cat	of catalyst
feed	of feedstock
i	of component i
j	number of the reaction
N_2	of nitrogen

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