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An experimental study of fluid catalytic cracking in a downer reactor

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Abstract

First results of an experimental study of the fluid catalytic cracking (FCC) process in a new type of reactor, the downflow gas–solids reactor or ‘downer’, are presented. A bench-scale experimental set-up has been constructed, the downer with an inner diameter of 25 mm and a length of 800 mm being the central part of it. As a first step in the development and characterisation of this reactor, catalytic cracking of cumene has been chosen as a model reaction. In a temperature range of 743–823 K, catalyst-to-oil (CTO) ratios up to 25 and residence times of 60–350 ms, conversions were between 10 and 70%. Comparison to modelling results, on the basis of a plug flow model, showed that the measured conversions were lower than expected on the basis of the calculations. The higher the solids mass flux, the greater the difference between the two, indicating that incomplete break-up of the solids stream entering the downer — with particle clusters negatively affecting transfer processes to and from the individual particles — might be the cause for these reduced conversions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cracking; Plug flow; Downer reactor

1. Introduction

Nowadays, a riser with co-current upward flow of gas and solids is the standard reactor for the industrial fluid catalytic cracking (FCC) process. This reactor type, however, suffers from several disadvantages, such as backmixing of particles along the reactor walls due to gravity, particle clustering and radial solids segregation, resulting in a wide solids residence time distribution. This, again, may lead to gasoline yields that are lower than theoretically attainable. A characteristic demand for the FCC process is a very short, but uniform contact time between the catalyst particles and the gas, which is necessary to obtain the desired product distribution and to avoid excessive coke formation. In future, this will become even more important, since increasingly active catalysts are being developed, which characteristically have a very high activity but also show fast deactivation due to fast production of coke.

To overcome the disadvantages of conventional riser reactors, an increasing interest in gas–solids downflow reactors (‘downers’) can be seen in the literature over the last years. Several investigations of the fluid dynamics of downers have confirmed that — in comparison with risers — the two-phase flow is much more uniform in radial direction. Furthermore, it has been found in experiments that backmixing of solids is strongly reduced, which corresponds to narrower solids residence time distributions and allows much shorter residence times [1,2]. Essential for optimum reactor performance is the fluid dynamic behaviour of the gas–solids flow. At first, the solids flow is a compact stream with small surface area per unit mass. Due to momentum transfer from the gas to the solids, the solids stream breaks up. During this break-up phase, relative velocities are high, promoting heat and mass transfer. Eventually, a steady situation is reached, with the solids flowing at a constant velocity. In the ideal case, a homogeneous suspension flow is formed, with all particles moving separately at single particle terminal velocity. However, experiments show, that particle velocities often are much higher, which is explained by the fact that particles move in clusters [3]. The gas atmosphere within these clusters is supposed to be stationary and, consequently, comprises a resistance for transfer processes. Purpose of the current study is to investigate these particle cluster phenomena and relate them to reaction behaviour. Although fluid dynamic data of the downer, such as pressure profiles, velocity profiles of both solids and gas in axial and radial direction, are available in the literature, no clear picture of the solids flow structure, especially in the first — determining — part of the downer, has been obtained yet. Data on the reactor performance itself, e.g. conversion,

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Nomenclature

CTO	catalyst-to-oil ratio ($(\mathrm{kg\,s^{-1}})_{\mathrm{cat}}/(\mathrm{kg\,s^{-1}})_{\mathrm{C}}$)
E_{A1}, E_{A2}	activation energy of reaction 1 and 2 ($\mathrm{J\,mol^{-1}}$)
g	gravitational constant ($\mathrm{m\,s^{-2}}$)
k_1, k_2	reaction rate constants for reaction 1 and 2 ($\mathrm{s^{-1}}$)
k_{01}, k_{02}	pre-exponential factor of rate constant of reaction 1 and 2 ($\mathrm{s^{-1}}$)
Δl_{in}	length of solids path from silo exit up to reactor inlet (m)
M	molecular weight ($\mathrm{kg\,mol^{-1}}$)
R	gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	temperature (K)
t_{c}	contact time (s)
u_{p}	solids velocity ($\mathrm{m\,s^{-1}}$)
X_{tot}	total conversion (%)
X_{dealk}	conversion due to dealkylation (%)
y	mass fraction

Greek letters

α	deactivation constant ($\mathrm{s^{-1}}$)
τ	dimensionless time $= t/t_{\mathrm{c}}$
ϕ_{deact}	deactivation function

Subscripts

B	benzene
C	cumene
cat	catalyst
dIPB	(m-, p-)diisopropylbenzene
OP	other products
P	propylene

selectivity and yields, is still largely missing. The current experiments are intended to gain a better insight into gas–solids flow in downers through direct determination of the influence of flow conditions on reaction behaviour, omitting the step of measuring fluid dynamic properties.

2. Experimental set-up

Fig. 1 shows the flow sheet of the entire equipment. In a previous stage the set-up was tested and used for coal pyrolysis [5]; some major changes were necessary to accommodate FCC reactions. The ultra-short reactor residence times with narrow residence time distribution put strong demands on the experimental apparatus concerning solids feeding and gas–solids mixing at the downer inlet and separation of gas and solids at the downer outlet.

A newly designed device provides constant feeding of hot solids (up to 700°C). This combines a fluidised bed with a small silo at the exit. The fluidised bed was chosen for its high heat transfer coefficients and good solids mixing, thus avoiding local overheating. Heat is provided by means of electrical heating coils with a total electric power of 10 kW. At the exit of the silo an orifice is used that can be exchanged to accommodate a range of mass flows by using different orifice diameters. After calibration, the mass flow can be calculated from the on-line measurements of the pressure difference over the orifice. This mass flow depends amongst others on the height of the fluidised bed, which is kept constant by feeding solids with a loss-in-weight screw feeder. Results from this feeding unit were satisfactory: a continuous mass flow with fluctuations in the order of less than 5% on a time scale of 20 ms was obtained.

The oil is vaporised and heated to a temperature of approximately 573 K and subsequently mixed into a heated N_2 flow; a homogeneous mixture is secured by means of a static mixing element.

A gas–solids mixing chamber is located directly upstream of the downer. The solids flow vertically along the central axis of the chamber and the gas flows radially inward through a highly-porous ceramic cylinder, before contacting the solids in the centre. The gas–solids flow, which is still inhomogeneous at this point, enters the downer reactor through a converging/diverging nozzle, where the solids stream is ruptured by the expanding gas flow and a more homogeneous solids suspension flow is created. The fluid dynamic conditions (such as gas velocity and solids mass flow) determine the position of the point at which a homogeneously dispersed flow is obtained.

The heart of the set-up is the downflow reactor, a ceramic tube with an inner diameter of 25 mm and a length of 800 mm. Heat losses to the environment are minimised through temperature-controlled wall heating. However, heat input from the walls to the reacting flow is limited due to the small heat transfer area available. Thus, the heat that is required for the endothermic cracking process must be supplied mainly by the reactants.

After reaction, the two-phase flow exiting the downer flows through a cooling section to a conventional cyclone, where the catalyst is separated from the product gas flow. The gaseous products can be incinerated and leave through the stack. At the reactor exit part of the product flow is sampled continuously over a filter (to separate the catalyst and avoid further cracking) and led to the analysis section. The filter is exchanged and cleaned after each experiment. All tubing is kept at 463 K to prevent condensation of heavier components. A gas chromatograph Varian 3800 (capillary column, 30 m × 0.53 mm × 1.5 μm, methylpolysiloxan) with FID detector is used to analyse the product gas composition. The GC was equipped with a sample valve with 12 loops to enable quick sampling while analysis time was around 8 min. The product gas composition was normally determined from the average of 3–5 analyses. The spent catalyst was collected for coke (C, H) analysis in a LECO instrument.

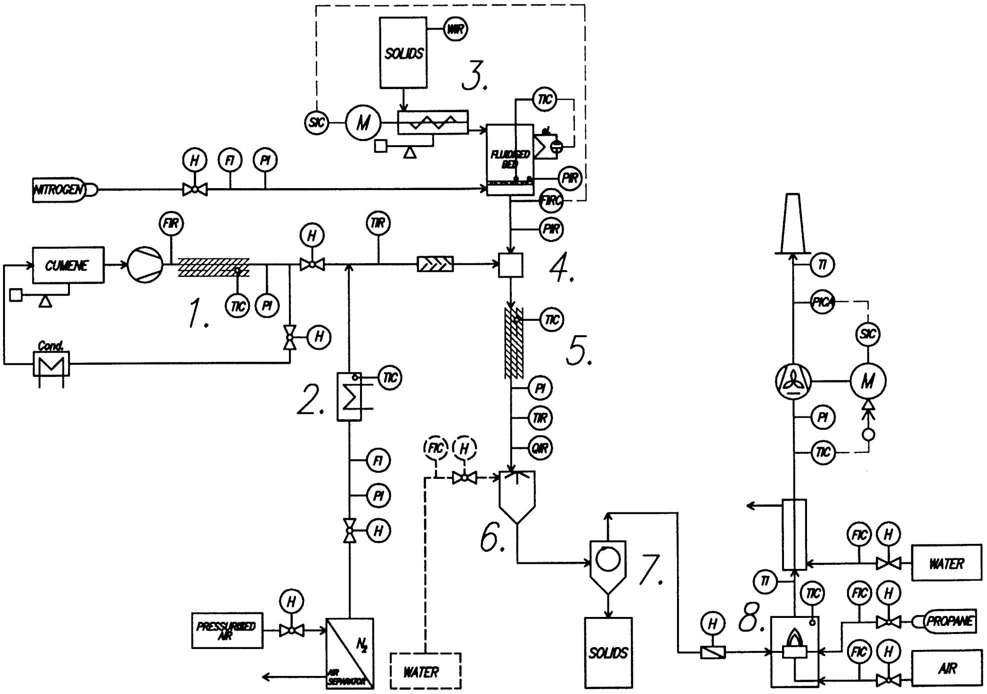

Fig. 1. Flow sheet of the downer set-up: 1, oil vaporiser; 2, nitrogen preheater; 3, solids heating and feeding device (loss-in-weight feeder with heated fluidised bed); 4, mixing chamber; 5, downer reactor; 6, quench; 7, cyclone; 8, product gas burner.

3. Experimental conditions

As a first step in development of a downer for the FCC process, a model reaction was chosen, viz. catalytic cracking of cumene, so that the analysis of the product flow is simplified substantially. Cumene has often been used as a model compound in testing of FCC catalysts. Cracking is very selective, producing primarily benzene and propylene. The reaction is representative for the aromatic fraction in gas oil and is catalysed by acid sites on the catalyst surface which are of intermediate acid strength [4]. The most important side reaction is the disproportionation of cumene, resulting in diisopropylbenzene. Thus, the reactions considered are

$$C_6H_5\text{–}C_3H_7 \rightarrow C_6H_6 + C_3H_6 \qquad (1)$$

$$2C_6H_5\text{–}C_3H_7 \rightarrow C_6H_6 + C_6H_4\text{–}(C_3H_7)_2 \qquad (2)$$

Aiming at a broad range of conversions, experiments were carried out at reactor outlet temperatures between 743 and 823 K, at catalyst-to-oil (CTO) ratios ranging from 8 up to 25 and at reaction times (gas residence times) between 60 and 350 ms. The catalyst was heated up to 973 K at maximum, while the gas flow was heated to approximately 573 K. The CTO ratios correspond to solids loading ratios ($\text{kg}_{\text{cat}}\,\text{kg}_{\text{g}}^{-1}$) between 1 and 10, whereas the average solids mass flux is in the range 4.5–14 $\text{kg}\,\text{m}^{-2}\,\text{s}^{-1}$. The partial pressure of cumene was kept low, between 2 and 13 kPa (at atmospheric reactor pressure). Gas velocities at the reactor inlet were in the range from 2 up to 12 $\text{m}\,\text{s}^{-1}$. Contact or reaction times were calculated on the basis of the reactor outlet temperature, neglecting gas expansion during the reaction. Since the partial pressure of cumene was low, this gas expansion was 2.5% on average and 9% at maximum (from calculation). The temperature of the gas changed while flowing through the reactor due to the heat input from the catalyst particles on the one hand and due to the endothermic cracking reaction on the other hand. However, it was assumed that the reactor was isothermal (at reactor outlet temperature). Because the reactor length was fixed, reaction times could be varied only by changing the gas velocity. The solids velocity at the reactor inlet was estimated from the following simple correlation (acceleration under the influence of gravitation, no friction):

$$u_{\text{p}} = \sqrt{2g\Delta l_{\text{in}}} \qquad (3)$$

With an entry length of 0.6 m the inlet solids velocity was approximately 3.4 $\text{m}\,\text{s}^{-1}$. In the majority of the experiments, the gas was travelling faster than the particles at the reactor inlet.

The catalyst used in this series of experiments was a typical equilibrium catalyst from an industrial FCC unit, which was used without further treatment. Some characteristic properties are given in Table 1. The median particle size was 82 μm, whereas the percentage of fines was very

Table 1
Properties of the industrial equilibrium FCC catalyst used

ρ_{p} ($\text{kg}\,\text{m}^{-3}$)	1500	MAT activity (%)	67
ρ_{b} ($\text{kg}\,\text{m}^{-3}$)	915	CRC (wt.%)	0.04
Pore volume ($\text{cm}^3\,\text{g}^{-1}$)	0.052	Ni (ppm)	4316
Surface area ($\text{m}^2\,\text{g}^{-1}$)	138	V (ppm)	5941

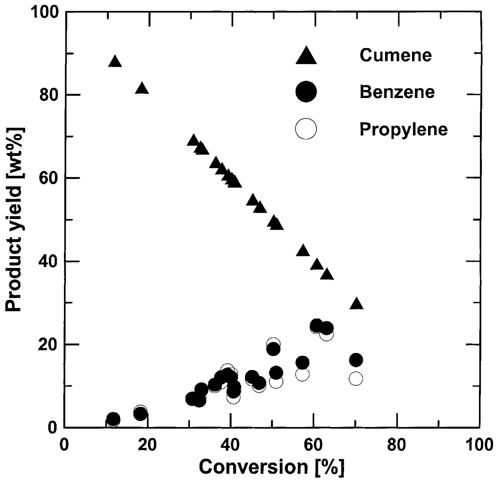

Fig. 2. Product yields as a function of total conversion.

small (less than 5 wt.% smaller than 40 μm). Cumene (Fluka, purity > 98%) was used without prior treatment.

4. Results and discussion

Fig. 2 presents the yields of the main reaction products as a function of the total conversion, where total conversion is defined as

$$X_{\mathrm{tot}}\,(\%) = \frac{y_{\mathrm{C,in}} - y_{\mathrm{C,out}}}{y_{\mathrm{C,in}}} \times 100 \qquad (4)$$

In the aforementioned range of experimental conditions total conversions ranged from 10 up to 70%.

$y_{\mathrm{C,in}}$ was estimated on the basis of the product gas composition, since it was not yet possible to measure this quantity directly (e.g. with a tracer gas). As a measure for the accuracy of the experimental data, the mass balance of each experiment was evaluated indirectly by calculating balances for C, H and aromatics (coke was not accounted for). Calculation of an aromatics balance was allowed since it is known from literature that the aromatic ring is not cracked [6]. Deviations in all balances were within 5 mol%, which was considered satisfactory. Figs. 3–5 show the (total) conversion as a function of the three main parameters, temperature, reaction time and CTO ratio. It is seen that a higher temperature results in a higher conversion. Longer residence times and higher CTO ratios also lead to higher conversions, as could be expected.

To calculate the conversion that is exclusively due to the dealkylation reaction, the following equation was used:

$$X_{\mathrm{dealk}}\,(\%) = \frac{(y_{\mathrm{B,out}}/M_{\mathrm{B}}) - (y_{\mathrm{dIPB,out}}/M_{\mathrm{dIPB}})}{y_{\mathrm{C,in}}/M_{\mathrm{C}}} \times 100 \qquad (5)$$

Results for the conversion due to dealkylation as a function of the total conversion are presented in Fig. 6. It is clearly visible, that in the current experiments other reactions than dealkylation do play a major role. Apart from the experimental data of the current studies, the figure shows data from literature as well (catalytic cracking of cumene in a downer [8,9]). Here, too, conversion due to dealkylation is much lower than the total conversion, although somewhat higher than in the current work. The test data in the microriser show that the reaction is very selective in this case. It is, however, not allowed to directly extrapolate the results to an industrial riser, since the far more complex flow phenomena in a large-scale unit, with for example the already mentioned phenomenon of solids backmixing, result in a much lower selectivity.

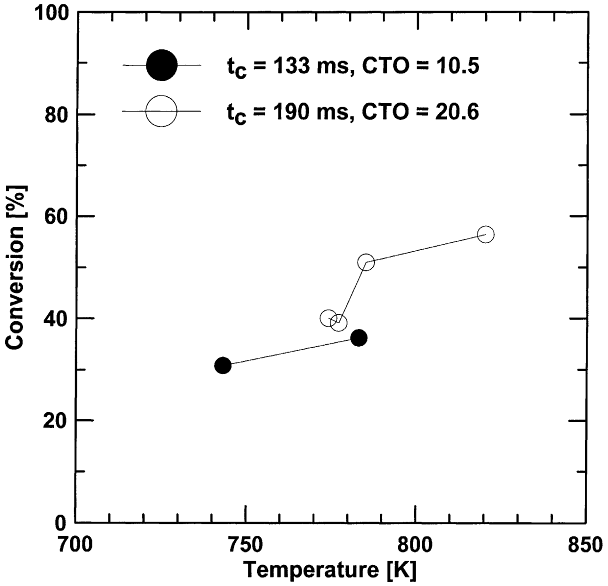

Fig. 3. Conversion as a function of reactor temperature.

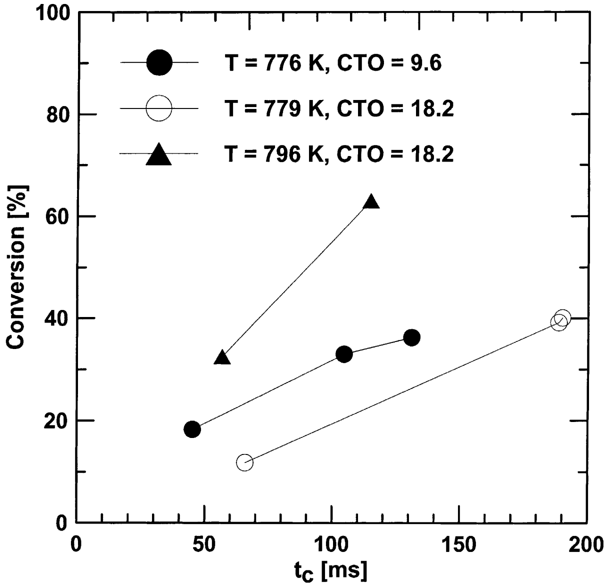

Fig. 4. Conversion as a function of contact time.

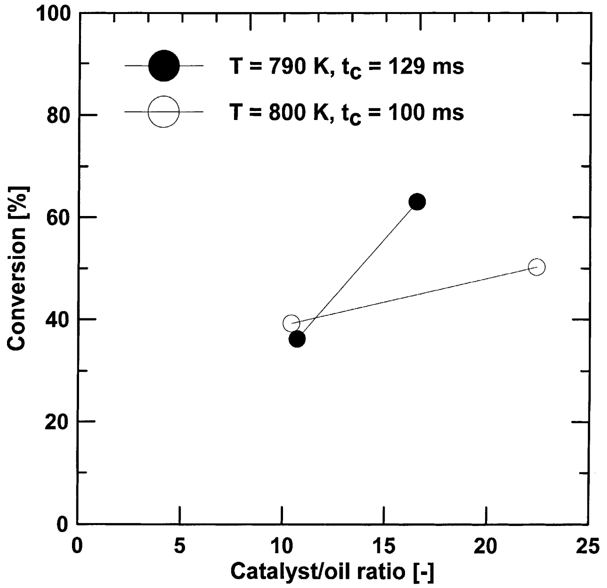

Fig. 5. Conversion as a function of CTO ratio.

Apart from propylene and benzene, ethylbenzene is formed as a major side product, whereas other side-products are found in only minor amounts. Ethylbenzene is a product that results primarily from thermal cracking. This indicates that in the current tests thermal cracking plays an important role.

Fig. 7 depicts the coke yields, which were very high, up to 19 wt.% (as fraction of the feed). This is at least partly explained by the fact that the catalyst could not be stripped in the current set-up. As was already indicated above, it was not yet possible to determine a mass balance over the reactor in absolute quantities. Thus, these data must be regarded with care and cannot be compared directly with data from other test units. Nevertheless, some trends are visible. A higher conversion leads to a higher coke yield. Contact time was found to be the major factor responsible for this increase (Fig. 7). A higher CTO ratio also results in an increase of the coke yield, whereas an influence of the temperature was not found. Coke-on-catalyst (or delta-coke, the amount of coke formed on the catalyst in the cracking experiment, expressed as weight fraction) was found to decrease slightly at higher CTO (Fig. 8). This is in agreement with expectations based on riser technology.

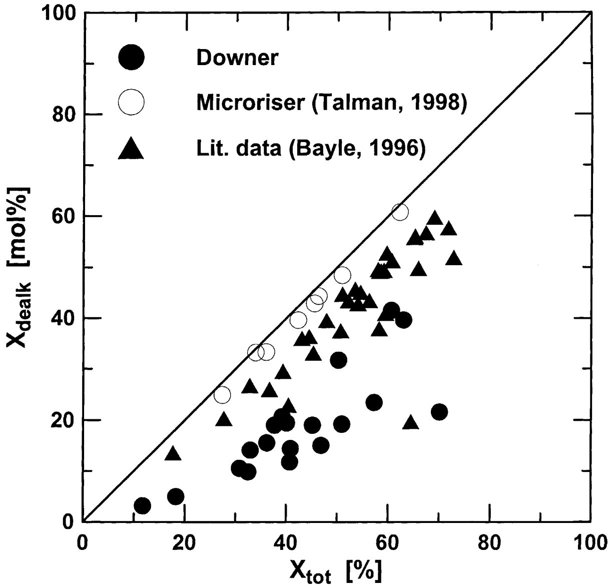

Fig. 6. Comparison of X_{tot} and X_{dealk}: downer data compared with data obtained in a laboratory riser reactor [7] and with data from a downer study presented in [8].

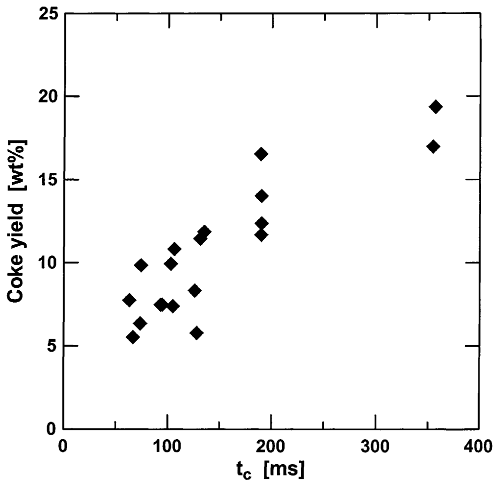

Fig. 7. Influence of contact time on coke yield (as weight fraction of feed).

4.1. Modelling

On the basis of former experiments with the same reaction system (same catalyst/cumene) in a novel test reactor,

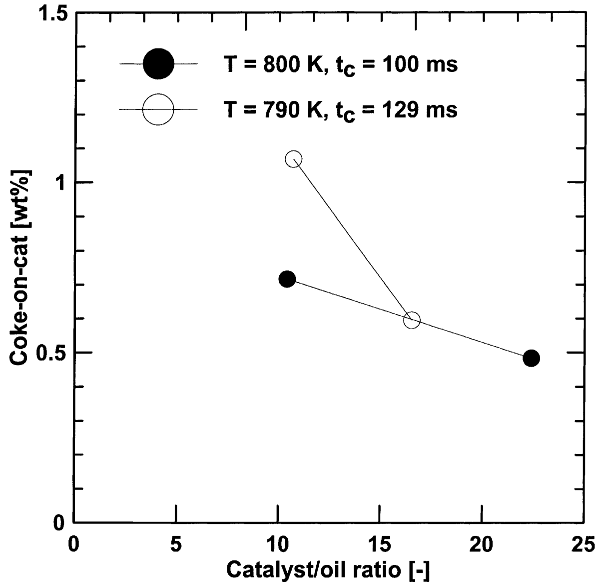

Fig. 8. Coke-on-catalyst as a function of CTO ratio.

the microriser [10], a simplified kinetic model was formulated. This model incorporates the dealkylation and disproportionation of cumene (according to Eqs. (1) and (2)), with the following reaction kinetics:

$$-r_C = k_1 y_C + k_2 y_C^2 \tag{6}$$

$$k_1 = k_{01} \exp\left(-\frac{E_{A1}}{RT}\right) \text{ and } k_2 = k_{02} \exp\left(-\frac{E_{A2}}{RT}\right) \tag{7}$$

$$\phi_{\text{deact}} = \exp(-\alpha t_c \tau) \tag{8}$$

Thus, the dealkylation was modelled as a first order reaction, whereas the disproportionation was considered to be of second order. The Arrhenius equation was used for the reaction rate constants. Catalyst deactivation was modelled as a function of particle residence time according to Froment and Bischoff [11]. The parameters that were determined on the basis of the experiments were: $k_{01} = 286\,\text{s}^{-1}$, $k_{02} = 0.292\,\text{s}^{-1}$, $E_{A1} = 42.3\,\text{kJ mol}^{-1}$, $E_{A2} = 10.1\,\text{kJ mol}^{-1}$ and $\alpha = 5.52 \times 10^3\,\text{s}^{-1}$. These values indicate that the initial selectivity for dealkylation is very high. The value of the activation energy of dealkylation is somewhat lower than found in most other studies [12], but does correspond to that given in a recent study [8]. The value of the deactivation constant is very high and not realistic (a half-life time of 0.12 ms), its determination in the microriser tests was not very reliable due to lack of sufficient data. However, in the range of the current experimental conditions, the model describes the data well, with an average deviation of 6%.

In a first step towards modelling of the downer, the problem was considerably simplified by assuming that the plug flow model in combination with the pseudo-homogeneous approach was valid, leading to the following set of differential equations:

$$\frac{dy_C}{d\tau} = -(k_1 y_C + 2k_2 y_C^2)\frac{\dot{m}_{\text{cat}}}{\dot{m}_C}\phi_{\text{deact}} \tag{9}$$

$$\frac{dy_B}{d\tau} = (k_1 y_C + k_2 y_C^2)\frac{\dot{m}_{\text{cat}}}{\dot{m}_C}\phi_{\text{deact}} \tag{10}$$

$$\frac{dy_P}{d\tau} = (k_1 y_C)\frac{\dot{m}_{\text{cat}}}{\dot{m}_C}\phi_{\text{deact}} \tag{11}$$

$$y_{OP} = 1 - y_C - y_B - y_P \tag{12}$$

With the fitted values of the model parameters, conversions in the downer can be predicted and compared to the experimental values. Fig. 9 presents the results for calculated versus experimental conversions. In most cases the calculated values are substantially lower than the experimental values. In those cases where experimental and calculated values are in close agreement, the solids mass flux is small.

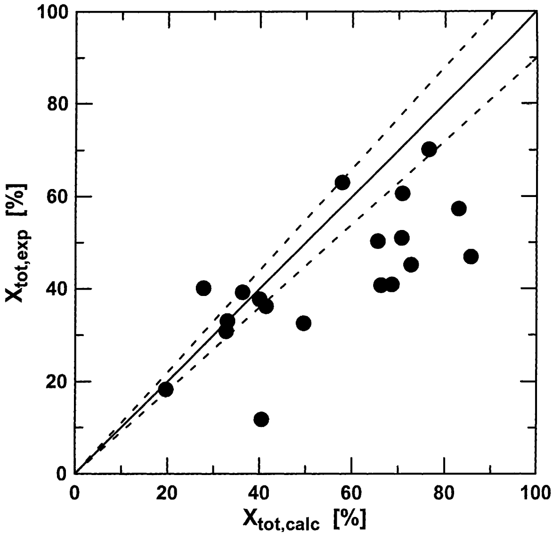

Fig. 9. Comparison of experimental and calculated values of total conversion (dashed lines represent 10% deviation in either direction).

Here, only a qualitative explanation is given. In the simple downer model, the gas–solids flow is assumed to be a homogeneous suspension flow (pseudo-homogeneous approach). This assumption is allowed only when the heterogeneous reaction mixture can be regarded as homogeneous, i.e. a homogeneous gas–solids mixture with flat radial profiles of concentrations and temperatures and without intra-particle resistance (and resulting intra-particle gradients). Although, the radial profiles of solids velocity, concentration and mass flux in the downer are very flat — much flatter than in riser reactors at similar conditions [1,13] — and intra-particle resistances can indeed be neglected due to the small particle size, it is known from literature that particle clusters are present in the downer [14,15]. These particle clusters move at velocities higher than the single particle terminal velocity (due to reduced drag per unit weight), thus improving heat and mass transfer. At the same time, however, the gas atmosphere inside of the particle clusters is stationary and thus comprises an (extra) resistance to heat and mass transfer. Besides, the surface area available for transfer is strongly reduced. The lower the solids mass flux at a given gas velocity (or solids loading), the better the dispersion will be, thus explaining the fact that in the experiments with small solids mass flux the experimental data are close to the calculated values, whereas at higher solids loading ratios this agreement can no longer be observed.

Further measurements are required to come to a quantitative description of these particle clustering phenomena and their influence on reaction behaviour. In a longer downer, these effects might be strongly reduced, since, several experimental investigations have shown that a homogeneous dispersion is attainable after a certain downer length, even at very high solids loading ratios [16–18]. However, in the downer test facility in its current form, it is not possible to make an extension to the downer to further investigate this aspect. Concluding, and extrapolating to industrial-scale downer reactors, it can be stated that attention should be paid to clustering phenomena, especially in the design of the downer inlet. Through appropriate design, the entry length with not yet fully dispersed gas–solids flow can be minimised and clustering may be largely avoided.

5. Conclusions

A new bench-scale downer test unit for FCC was developed and a first series of experiments with catalytic cracking of cumene was carried out. The experiments demonstrated the specific downer features of extremely short residence times (60–350 ms) and high CTO ratios (up to 25, with even higher values attainable). Even at those short residence times, conversions were between 10 and 70% at temperatures between 743 and 823 K. Comparison of the experimental data with data calculated on the basis of known reaction kinetics and assuming plug flow showed that experimentally determined conversions were lower than predicted by the model in most cases, agreement was worse at higher solids mass flux. This indicates that the gas–solids flow in the downer was not homogeneously dispersed. Incomplete break-up of the compact solids stream at the downer inlet and particle clustering lead to a reduced exchange surface area and an (extra) resistance for mass transfer to the individual particles. This, again, results in a conversion that is considerably lower than expected on the basis of a pseudo-homogeneous reactor model.

Acknowledgements

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