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THERMAL CRACKING OF RECYCLED HYDROCARBON GAS-MIXTURES WITH HIGH OLEFINS CONCENTRATIONS IN THE FEED: OPERATIONAL ANALYSIS OF INDUSTRIAL FURNACES

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Simulation studies of thermal cracking of recycled hydrocarbon gas mixtures are presented. Due to their relatively high unsaturated content these types of mixtures show behaviour in cracking furnaces different from that of their saturated homologues. The detailed mathematical and kinetic model developed was validated by using the process control laboratory cracked gas analysis of an industrially operated cracking furnace. The effects of different feed compositions and those of operating parameters are also examined. It is shown that the radiant coil temperature profile, online operation period of the furnace, and the yield of the main products are different at various unsaturated concentrations in the feed. The influence of the radiant section residence time is also presented. Simulation results compared with the experimentally measured data of an industrially operated cracking furnace show good agreements.

Keywords: Pyrolysis, hydrocarbons, gas-mixtures, olefins, modelling, simulation

Introduction

Thermal decomposition of hydrocarbons has been studied for more than 70 years. Nevertheless, less attention has been paid on cracking behaviour of olefins since recycling of certain cracked gas-fractions has become important only in past one-two decades. While repyrolysis of formed ethane and propane has been applied for long, recycling of C4 and/or C5 fractions has only been introduced into industrial experience parallel with decreased market demand for plastics produced from butadiene and isoprene.

Sundaram and Froment [1-3] developed kinetic models for thermal decomposition of gaseous hydrocarbons and their mixtures. Kinetic parameters presented in these schemes are still applicable for thermal cracking of individual hydrocarbons and mixtures up to C4. Van Damme *et al.* [4] and Froment *et al.* [5] compared the results given by their kinetic model with those obtained from industrial applications. Ranzi *et al.* [6], Froment e*t al.* [7] and Dente *et al.* [8, 9] presented the initial product distribution when cracking light hydrocarbons and prepared the first fundamental pyrolysis simulation model, the SPYRO. Willems and Froment [10] presented a method of calculation of frequency factors and activeation energies, while Dente and Ranzi [11] prepared a mathematical model for hydrocarbon pyrolysis reactions. More recently, Poutsma [12], Savage [13], Sadrameli and Green [14] presented the system of fundamental free radical reaction relevant to pyrolysis and mechanisms and kinetic modelling systems for hydrocarbon pyrolysis, respectively. Zou *et al.*, [15], Pleiers *et al.* [16] and Kopinke *et al.* [17,18] studied and presented coke formation rates that influence the online operation period of cracking furnaces.

The mentioned C4/C5 fractions are hydrogenated upstream the cracking furnaces. Olefin content of hydrogenation reactor effluent mainly depends on its catalyst performance and can vary between 3 and 30%. Yet, unsaturated ratio of the furnace feed can also be reduced by mixing fresh, saturated hydrocarbons into reactor effluent. These are mainly butanes and/or pentanes in practice but, according to our simulation results, mixing of ethane also looks to be a promising alternative.

This paper examines the effects of unsaturated components in the feed on product yields and online operation period of the furnace aiming the opportunities of harmonizing the operating parameters at different feed compositions. Results obtained by numerical experimentation using a computer model are compared with experimentally measured data of an industrially operated cracking furnace.

Mathematical model

The kinetic model

Starting from the detailed composition of fed hydrocarbons and cracked gases a reaction network was built up with participation of all theoretically supposed ones in the first step of modelling, number of which was closely five hundred. As the second step, kinetic parameters were assigned to each reaction, source of which was the large amount of published literature data. If the published system was found to have been similar to the one examined by us, these parameters could be directly adopted [2, 3, 7]. In cases different from that, parameters were collected from other sources then interpolated or extrapolated on basis of analogy rules between the reactions in the same group [1, 4-6, 8, 9-15]. Of course, a comparison was made in the first case as well. The aim of these two steps was to build up a 'first generation' kinetic model that could reproduce measured yield data as accurate as possible.

Validation of the model was performed by comparing the results with those obtained experimentally from cracked gas analysis of an industrially operated furnace. This means that a set of multiply verified data, among stabilized operational circumstances, were collected in concert with the sampling schedule and procedure. Received yield data were not averaged but those in coincidence were taken as reference. Secondly, influence of each reaction to the yield-structure was examined. Effect of those to the yield structure was negligible could be deleted from the system with simplification purposes and for the reasons mentioned earlier. Having performed these procedures, 239 reactions remained in the examined system, kinetic parameters of which were fitted to the measured yield data in case of each reaction, except those leading to coke formation (coke 'yield' could not be measured). The fitting was performed in such a way that the trend of a product yield or consumption of a feed component was drawn as a function of modification of parameters (*A* or *E*). *Table 1* presents a part of arrangement of frequency factors from different sources together with the adopted ones in the first phase of modelling and with the ones fitted during validation of the model. *Fig. 1* shows an example of fitting the activation energies to experimentally measured yields at reactions of the prepared network.

Table 1: Assigning frequency factors (A, sec^{-1} or $cm^3*mol^{-1}*sec^{-1}$) to reactions in the system

Reaction	Literature data sources				Adopted	Fitted
$C_3H_8 \rightarrow CH_3* + C_2H_5*$	$7.1\cdot10^{16\mathbf{c}}$	$2\cdot10^{16\ \mathbf{h}}$	$1.3\cdot10^{16\mathbf{j}}$	---	$3\cdot10^{16}$	$2.2\cdot10^{16}$
$n\text{-}C_4H_{10} \rightarrow 2\ C_2H_5*$	$5\cdot10^{16\ \mathbf{c}}$	$1.5\cdot10^{16\mathbf{h}}$	---	---	$2\cdot10^{16}$	$2.5\cdot10^{16}$
$C_3H_8 + CH_3* \rightarrow CH_4 + 1(2)\text{-}C_3H_7*$	$1.5\cdot10^{9\mathbf{c}}$	$3.4\cdot10^{10}$ $(4\cdot10^{9})^{\ \mathbf{h}}$	$10^{8\ \mathbf{i}}$	$4.9\cdot10^{9}$ $(1.5\cdot10^{9})^{\mathbf{j}}$	$1.5\cdot10^{9}$ $(3\cdot10^{9})$	$2.2\cdot10^{9}$ $(4.2\cdot10^{9})$
$1\text{-}C_3H_7* \rightarrow C_2H_4 + CH_3*$	$5\cdot10^{13\ \mathbf{c}}$	$4\cdot10^{13\ \mathbf{h}}$	$5\cdot10^{13\ \mathbf{k}}$	$10^{14\ \mathbf{i}}$	$5\cdot10^{13}$	$4.4\cdot10^{13}$
$CH_3* + C_2H_5* \rightarrow C_3H_8$	$10^{10\ \mathbf{c}}$	$3.2\cdot10^{9\mathbf{h}}$	---	---	$5\cdot10^{9}$	$3.2\cdot10^{10}$

Sources in Table 1 are indicated as follows: **c** – Dente and Ranzi (1983); **d** – Zdenek *et al.* (2003); **h** – Sundaram and Froment (1978); **i** – Ranzi *et al.* (1997), **j** – Willems and Froment (1988); **k** – Ranzi *et al.* (1983)

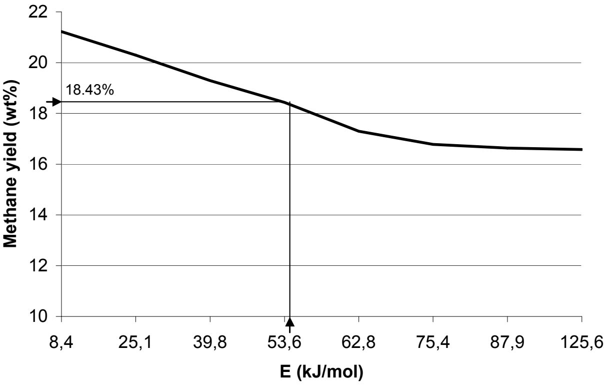

Figure 1: Variation of methane yield as a function of activation energy in case of reaction: $C_2H_4 + CH_3* = C_2H_3* + CH_4$

The reactor model

The geometry of the furnace coil and high Reynolds-numbers used in thermal decomposition process enable tubular reactor and plug-flow assumptions. As a consequence, mass, energy and momentum balances can be written as follows [19].

Mass balance:

$$\frac{\partial c_i(x,t)}{\partial t} = \sum_{k=1}^{N_r} \alpha_{ki} r_k(\boldsymbol{c},T) - v\frac{\partial c_i(x,t)}{\partial x} \tag{1}$$

$$i = 1 \rightarrow N_c,\ k = 1 \rightarrow N_r$$

where c_i is the concentration of reactant *i*, *x* is the axial distance along the reactor, *v* denotes the cracked gas convective velocity, r_k is the rate of the reaction *k*, and α_{ki} stands for the stoichiometric coefficient of component *i* in the reaction *k*. N_c denotes the number of species, while N_r stands for the number of reactions.

Enthalpy balance:

$$\begin{aligned}&\left(\sum_{i=1}^{N_c} C_{pi} c_i\right)\frac{\partial T(x,t)}{\partial t} = \sum_{k=1}^{N_r}(-\Delta H_k)\, r_k(\boldsymbol{c},T) - \\ &-v\left(\sum_{i=1}^{N_c} C_{pi} c_i\right)\frac{\partial T(x,t)}{\partial x} + U\left[T_{fb} - T(x,t)\right]\end{aligned} \tag{2}$$

where T is the cracked gas temperature, C_{pi} is the heat capacity of species i, ΔH_k denotes the heat of reaction k, U denotes the overall heat transfer coefficient from the fire box to the cracked gas, d_t is the inner diameter of the reactor tube, and T_{fb} stands for the temperature of fire box.

The pressure drop along the radiant pipe:

$$\frac{dp}{dx} = \left(f\,\frac{L_t}{144 d_t g} + \xi(x)\right)\frac{\rho v^2}{2} \tag{3}$$

where p denotes the pressure, ρ is the density of gas mixture, L_t the equivalent pipe length, g is acceleration due to gravity, $\xi(x)$ is the local resistance coefficient of reactor tube junctions or bends, and f denotes the friction factor which is calculated using the expression for smooth pipes:

$$f = \frac{0.3164}{Re^{0.25}} \tag{4}$$

The balance equations are solved subject to boundary and initial conditions:

$$c_i(x,0) = c_{i0}(x) \quad i = 1 \to N_c, \quad T(x,0) = T_0(0) \tag{5}$$

$$c_i(0,t) = c_{i.in}(t) \quad i = 1 \to N_c, \quad T(0,t) = T_{in}(t) \tag{6}$$

The computer model

The reference furnace consists of a radiant and a conection section, as well as of six transfer line exchangers (TLE) with one steam drum. Firing in radiant section is performed by sidewall and floor burners where natural gas is burnt which is also mixed with the methane fraction formed in cracking process. Preheating of feed and dilution steam as well as preheating and super-eating of high-pressure steam takes place in convection section. Between the feed preheater and steam super-heater a boiler-feed-water preheater is placed. The furnace was designed to assure uniform distribution and 'drive' of different streams to convection-section heat-exchanger bundles. Furnace feed streams are collected in two places and distributed into 96 radiant coils by Laval-nozzles. After a certain length two small-diameter (39 mm) coils unify in a bigger one (57 mm). According to this, the furnace contains 48 radiant coils connected to one TLE by eight as it shown in *Fig. 2.* The residence time of reaction mixture in the radiant section is very short (0.3 sec.).

Having identified the kinetic parameters, simulations were performed by CHEMCAD computer simulator that was chosen for its large thermochemical database as well as for the fact that not only molecules but radicals can also be created and handled. As a further part of its implementation, geometrical data were given according to the technical drawings of the examined industrial furnace. Data input of parameters and process-variables were also performed on basis of industrial circumstances.

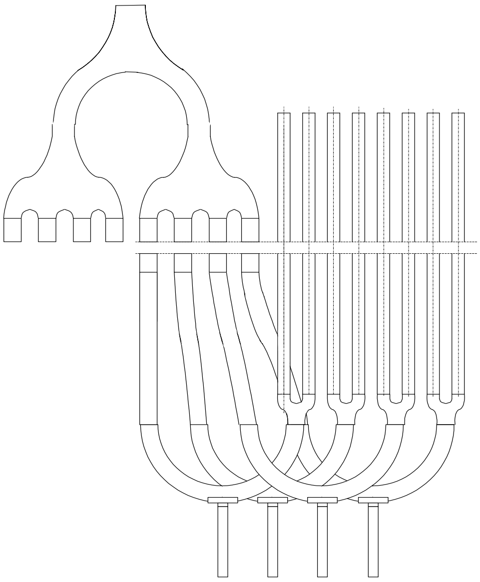

Figure 2: Radiant coil arrangement

So as to determine composition of cracked gases at the furnace outlet the following input data are needed:

a.) feed composition by component and its flow-rate
b.) inlet and outlet temperatures (COT) of the furnace
c.) pressures at inlet and outlet (to calculate pressure-drop along the coil)
d.) hydrocarbon/dilution steam ratio and steam flow-rate
e.) coil geometry, i.e. the lengths and internal diameters of segments
f.) temperature-profile along the coil or heat-transfer coefficient (U), with tube metal temperature (TMT)
g.) each chemical reaction taking place in the system with their kinetic parameters (activation energies and frequency-factors, respectively)

Operating parameters of the furnace (points a – d), such as temperatures, pressures, flow rates are monitored by an Advanced Process Control system (APC) and they can be registered in accordance with feed- and cracked gas analysis [20].

The factor of losses depends on convectional circumstances dominant in the pipe (*Re*-number) and its shape. According to this, the total pipe length (point e) is the sum of straight segments and the equivalent pipe length.

Table 2 presents comparison of measured and simulated yield data with fitted kinetic parameters.

Experimental: Application and presentation of simulated results

Having validated the model, series of simulations were performed with the purpose of examining the effect of different feed components on product yields. Some typical feed compositions are shown in *Table 3.*

The influence of the n-butane concentration is shown in *Table 4.*

As it is seen, 28% higher n-butane concentration is needed to achieve 4% increased ethylene yield but the relative coke formation rate was decreased by almost 25%. This decline is also due to the lower relative concentration of olefins in the feed, i.e. because of less coke precursors. Neither the yield of methane nor that of propylene varies significantly but less aromatic compounds (BT) are produced. In conclusion, when increased olefin content occurs in the feed adding more butane into it appears to be economically reasonable since higher furnace run-length can be reached in parallel with the possible decreased hydrogenation reactor load that also leads to depression of olefin content in the feed.

Table 2: Comparison of the measured and simulated product yields with fitted kinetic parameters

Component/ Yields (wt %)	**Measured 1**	**Fitted 1**	**Measured 2**	**Fitted 2**	**Measured 3**	**Fitted 3**
Hydrogen	1.06	0.98	1.05	0.98	0.98	0.96
CO	0.10	0.11	0.06	0.07	0.05	0.07
Methane	18.72	18.67	18.53	18.64	18.27	18.52
Ethane	3.39	3.34	3.56	3.51	3.63	3.53
Ethylene	30.64	30.58	31.13	31.08	32.30	32.17
Propylene	19.51	19.64	19.54	19.61	19.26	19.37
n-butane	8.50	8.58	8.57	8.63	10.08	9.87
Acetylene	0.51	0.55	0.51	0.56	0.50	0.49
Benzene	1.34	1.36	1.34	1.36	1.33	1.30
Toluene	0.22	0.25	0.22	0.25	0.22	0.25

Table 3: Some typical compositions of the furnace feed

Component (wt%)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Propane	0,8937	0,3251	0,1462	0,4315	0,0880
Propylene	0,7019	0,9518	0,1881	0,9308	0,3292
i-butane	12,5453	8,6917	6,5118	6,9339	5,2723
1-butene	0,8193	0,0716	0,1484	0,0891	0,0891
n-butane	61,9166	69,5411	67,6253	72,1629	63,9667
2-butene	2,4412	0,3452	0,3934	0,3899	0,4321
i-pentane	4,9792	6,4142	8,4320	5,9221	9,4355
2M-butene-1	0,2211	0	0,0655	0,0473	0,0843
n-pentane	5,8455	7,0751	8,2326	6,3494	10,8684
2-pentene	0,2306	0	0	0	0
2M-butene-2	1,7299	0,4041	0,5704	0,4425	0,7475
Cyclopentene	0,0874	0	0	0	0,0735
Cyclopentane	5,9247	5,4214	6,7055	5,7778	7,7222
2M-pentane	0,5752	0,6778	0,6036	0,4434	0,8912
∑ other C6	1,0885	0,0808	0,3773	0,0794	0

Table 4: Variation of product yields as a function of n-butane concentration in the feed

n-butane conc., wt%→ product yields, wt% ↓	**65.95** simulated	**65.95** measured	**72.35** simulated	**72.35** measured	**79.55** simulated	*79.55* measured	**86.71** simulated	**93.89** simulated
Hydrogen	0.88	0.92	0.89	0.94	0.91	0.99	0.95	0.98
Methane	18.54	18.71	18.14	19.32	18.11	19.18	18.02	17.96
Ethylene	30.58	30.61	31.02	31.21	32.21	32.42	33.43	34.43
Propylene	19.34	19.74	19.28	19.53	19.16	19.34	19.09	19.01
n-butane (residual)	8.92	8.77	9.28	9.17	9.75	9.68	10.07	10.38
Benzene + Toluene	1.78	1.73	1.61	1.58	1.41	1.37	1.28	1.19
Coke (theoretical)	0.0087	------	0.0084	------	0.0081	------	0.0075	0.0069

Further simulations were carried out at five different unsaturated concentrations in such a way that concentration of each component in the feed was varied proportionally. Rest of independent variables (COT, ST/HC) was kept constant. Simulated results are presented in *Fig. 3.* As Fig. 3 shows, trend of methane yield and that of propylene shows a linear decline with a rising unsaturated rate. Rising conversion of n-butane is only 'virtual' since its relative concentration in the feed also declines when the unsaturated concentration is higher. Nevertheless, variation of ethylene yield shows a slightly rising trend which, for the first sight, looks to be surprising. To find the explication, it was examined how the concentration of some key unsaturated feed components vary along the radiant coil. Parallel with this, their kinetic route was also followed. Variation of three feed components concentration, that are present in the highest amount in the feed, is shown in *Fig. 4.* Concentrations of 2M-butene-2, butane-1 and butane-2 are the most elevated in the feed so their kinetic routes were examined. All of them take part in chain-initiation, hydrogen-abstraction, chain-forwarding and recombination reactions [3]

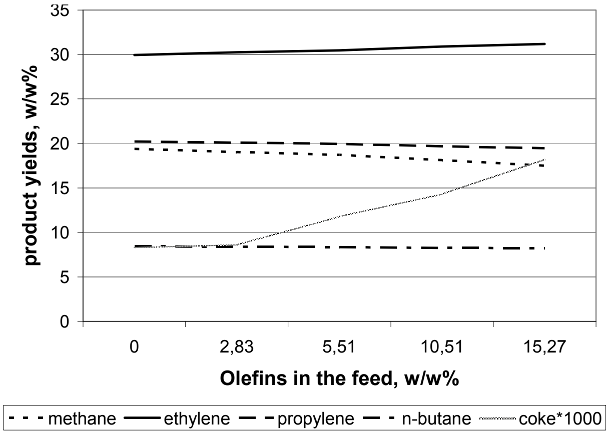

Figure 3: Variation of product yields as a function of olefin concentration in the feed

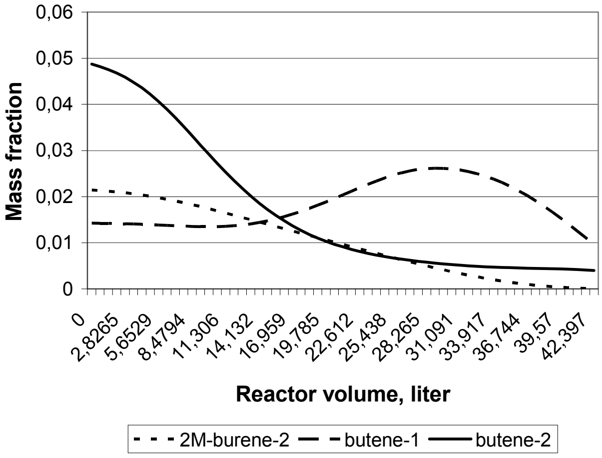

Figure 4: Variation of some olefins concentration along the radiant coil

Fig. 5 shows the temperature profiles in the first part of the radiant coil revealing the differences between those in case of cracking a C3-C6 mixture in a furnace with short residence time (0.3 sec) when the feed is free of olefins and when it contains 15% unsaturated components. This examination was initiated by some operational experiences observed in industrial plants according to which higher coke deposits were realized in the first part of radiant coil, causing a very short online operation time as well as cracking of coils in certain cases. The theoretical explication of this phenomenon is that unlike saturated hydrocarbons, all the olefins and diolefins contribute more to coke deposits in the first part of cracking coil. This is more pronounced the higher the reactivity of the component is. It is a question of profitability to operate the furnace at the lowest possible steam/hydrocarbon ratio since a lower steam rate reduces specific energy consumption of the production unit. Basically, one thing has to be decided: up to what extent this ratio can be reduced without having a significant negative effect on product yields and on furnace online period. *Table 5* shows that reducing the ratio by 20% practically has no influence on product yields but a shorter runtime can be expected because of higher coke formation rate.

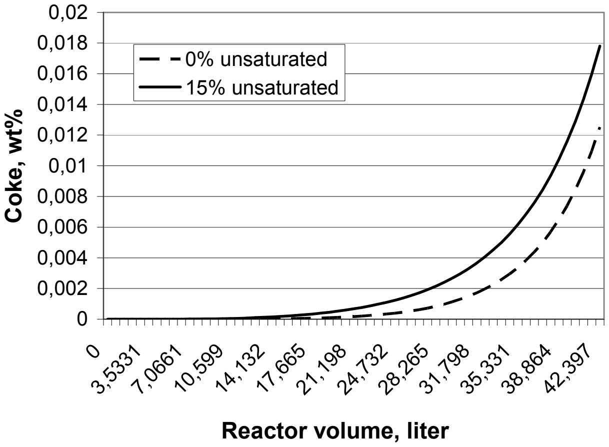

Figure 5: Formation rate of coke along the radiant coil

Fig. 6 shows the variation of formation rates of some undesired products, such as CO, coke and acetylenes along the radiant coil. As it is seen, formation of MAPD starts first and rate of coke formation increases exponentially at the last part of reactor pipe.

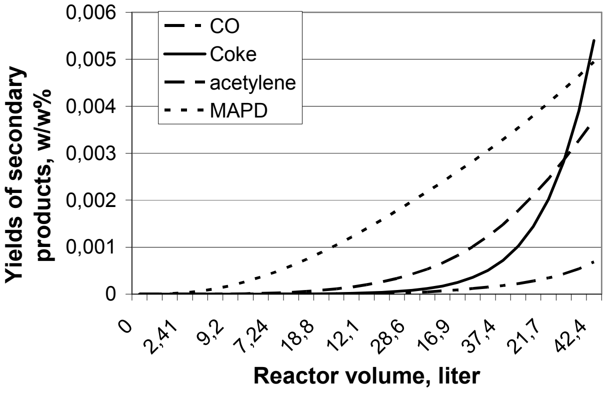

Figure 6: Variation of formation rates of some undesired products along the radiant coil

It should be noted that the effects of the dilution steam reduction cannot be simulated with high accuracy since catalytic effect of tube metals are not described by any known kinetics. Though the literature survey [15-18] shows a clear classification of coke precursors (such as olefins, acetylenes and aromatics) but there are no detailed discussions on dilution steam effect. Nevertheless, practical experience also confirms the data shown in Table 5.

Table 5: Simulation at different steam/hydrocarbon ratios

Steam reduced by...%	**5**	**5**	**10**	**10**	**15**	**15**	**20**	**20**
Temperature (COT), °C →	835	840	835	840	835	840	835	840
Product yields, wt%								
Methane	18.22	18.75	18.32	18.72	18.43	18.83	18.53	19.06
Ethylene	32.22	33.73	32.07	33.18	31.92	33.07	31.78	33.25
Propylene	20.63	20.15	20.68	20.34	20.74	20.38	20.79	20.32
Butadiene	3.97	3.85	3.97	3.89	3.98	3.89	3.98	3.86
n-butane (residual)	8.74	7.58	8.72	7.88	8.70	7.82	8.68	7.56
Benzene + toluene	1.61	1.63	1.71	1.64	1.75	1.66	1.81	1.69
Coke	0.016	0.019	0.017	0.018	0.017	0.018	0.018	0.019

According to the daily operational experience, for the relatively high unsaturated-content of the feed, online operation period of the furnace became shorter than the designed value, especially at the end of radiant coil lifetime. This is mainly due to the higher coke formation rate, which is caused by the elevated olefin content (coke precursors) in the feed and by those formed during the decomposition process. For these reasons, further alternatives were searched for to process the mixture in question more efficiently. Simulations with variation of radiant coil geometry, i.e. alteration of residence time were carried out to compare yield data and coke formation rate. Geometrical data of two existing furnaces (CF2 and CF3) were taken as reference so that the calculated residence times could be in real domain, i.e. 0.65 sec and 1.1 sec, respectively. It was supposed that a higher key-conversion and a higher ethylene yield could be reached, parallel with a reduced coke formation rate, when cracking these mixtures in furnaces with longer residence time. Simulations at similar feed compositions, total olefin content of which was 15.27%, were carried out with three values of COT and yield data were compared with those obtained from reference furnace. ST/HC ratio was adjusted similarly in all three furnaces. Results are shown in *Fig. 7.* As it was expected, a higher conversion of n-butane could be achieved both in CF2 and CF3 furnace than in the reference (CF1) furnace. Yield of ethylene is by 7% higher in CF2 and by 11.1% in CF3 at same COT. Though the coke formation rate is much bigger in both furnaces, by 21% and 32% respectively, this quantity of coke will be deposed on a five times higher surface in CF2 and on a ten times higher one in CF3. Taking into consideration the differences in residence times as well, it can be concluded that a 35-40% longer online operation period is expectable in case of both CF2 and CF3.

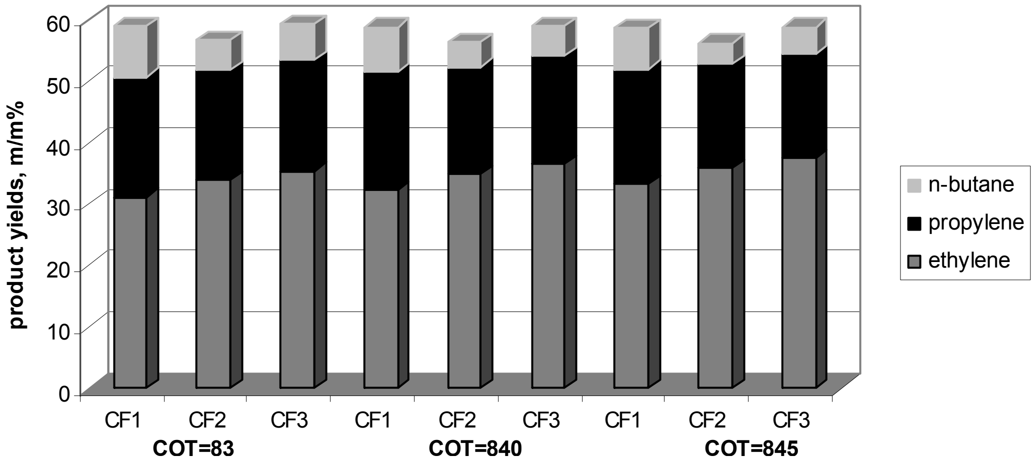

Figure 7: Yield comparison at furnaces with different residence time

Conclusions

When thermal cracking of recycled hydrocarbon gas mixtures occurs in industrial furnaces, the feedstock contains a relatively large amount of unsaturated components such as olefins and diolefins, a special attention has to be paid on coke formation since these compounds are coke precursors. The simulation study, carried out by means a computer model developed for examining thermal cracking of recycled gas mixtures, confirmed that variation opportunities originating from very different feed compositions can be harmonized well with operating parameters of the furnaces, with the purpose of achieving a maximum profitability. As it was shown, coke formation rate can significantly be reduced by decreasing olefin content of the feed. This can be done by mixing fresh hydrocarbons into the recycled streams like ethane and/or n-butane. According to industrial practice, recycled ethane is always available and n-butane is also worth to be purchased for this purpose. In conclusion, recycled streams cracking in furnaces with longer residence time looks to be a good alternative for olefin producers. Of course, the hydrogenation reactor upstream the cracking furnace as well as its catalyst has a main role in this complex process.

NOMENCLATURE

ΔH_k – heat of reaction k [J/mol]
A – surface area per unit axial distance [m^2]
c_i – concentration of reactant i [mol/m^3]
C_{pi} – heat capacity of species i [J/kg/K]
d – diameter of pipe/fitting [m]
f – friction factor [-]
g_c – acceleration of gravity [m/s^2]
L – equivalent pipe length [m]
N_c – number of species
N_r – number of reactions
r_k – rate of the reaction k [$mol/m^3/s$]
T – temperature of cracked gas [K]
t – time [s]
$\bar{t}$ – mean residence time [s]
T_{fb} – temperature of firebox [K]
U – overall heat transfer coefficient from the firebox to cracked gases [$W/m^2/K$]
V – convective velocity of cracked gas [m/s]
x – axial distance along the reactor [m]
α_{ki} – stoichiometric coefficient of component i in the reaction k
Δp – pressure drop [MPa]
ρ – density of cracked gas [kg/m^3]

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