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A Mechanistic Approach to Delayed Coking Modelling

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Abstract

The valorisation of oil distillation residues constitutes a major problem for refineries. Thermal processes like visbreaking and delayed coking are still quite diffused technologies. This paper presents some major aspects of the delayed coking kinetic modelling and some preliminary results compared with experimental data. A mechanistic approach has been adopted; it allows describing the process in wide ranges of operating condition and feedstocks. The developed model can be a useful tool for feedstock selection, production planning, control and optimisation. A special attention is devoted in the paper to substitutive addition reactions responsible of coke formation into the drums.

Keywords: Delayed Coking, mechanistic approach, molecular modelling, kinetic modelling, comparison with experimental data

1. Introduction

Several factors dictate the adoption of thermal processes in the refinery: i.e. product market demand, geographical area, refinery ownership policy etc. They are diffused world-wide thanks to their simple configuration and management, low cost and so on, when compared to catalytic processes. In the past a relatively scant attention has been devoted by the scientific literature to the kinetics and reactor modelling of these processes. Generally macro-kinetic models have been proposed, but they are not able to cover a wide range of operating conditions and feedstocks (Del Bianco et al. 1993, R. M. Filho and M.F. Sugaya 2001). Recently a mechanistic approach to liquid phase pyrolysis of hydrocarbon mixtures has been developed. A first application to the visbreaking has been presented (Dente et al. 1997). This paper deals with the extension of this approach to delayed coking modelling and with the peculiar aspects of this process. Delayed coking process is aimed to transform heavy hydrocarbon mixtures into more valuable products like gas, gasoline, kerosene, light and heavy gasoil (and coke).
A furnace connected to a system of coke drums (two or more alternatively operating) constitutes the typical unit (Figure 1). The feed enters in the furnace mixed with part of the bottom of the fractionator. This expedient is adopted in order to increase the

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◆ Author to whom correspondance should be addressed: giulia.bozzano@polimi.it vaporisation improving the heat transfer into the coils; however it is limited by the need of increasing the amount of crude transformed in the refinery. The coils are mainly aimed to pre-heat and vaporise the feed that substantially is transformed into the drum, which follows the furnace. The latter behaves as a semi-batch adiabatic reactor. The mesophase precursors gradually fill the drum. The vapour generated exits from the top. When the proper level in the drum is reached (for instance 60-70% of filling), the inlet stream is quickly switched to another one and the operation of coke removal starts.

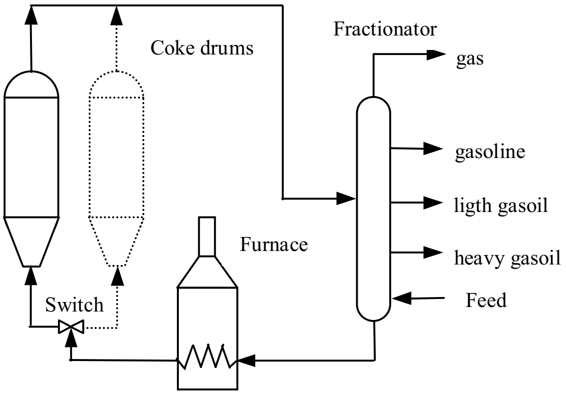

Figure 1. Schematic configuration of a delayed coking unit

The feedstocks used are of different origins: atmospheric or vacuum residues eventually mixed with heavy fractions coming from other treatments (e.g. decant oil), bitumens and so on. The preferred ones are vacuum residues. Of course a good characterisation of the feed is essential and very complex because of the feed nature. Details on the feedstock characterisation have been already reported in a previous paper (Bozzano et al. 1998). A peculiar aspect of delayed coking process is the high residence time into the drum (till 24 hours). It becomes progressively so extended that condensation reactions on aromatics, responsible of the coke formation, play more and more predominant role. This class of reactions is negligible in the visbreaking process due to its reduced residence time (about 10-30 minutes). The evaluation of substitutive addition reactions kinetic constants, together with the coking drum modelling, represents the main innovative aspect of the present model.

Incidentally condensation reactions are also important in forming coke deposits during hydrocarbon pyrolysis and generating soot in combustion processes (Bozzano et al. 2002). Therefore the mechanisms here reported can be useful in modelling coke formation in other processes.

2. Kinetic modelling

The maximum process temperature level (≤500°C), suggests that practically no significant reaction can take place into the vapour phase. Intramolecular radicals isomerisation can be neglected in the liquid phase. The thermal decomposition consists in a radical chain constituted by the following reaction classes: initiations, hydrogen abstraction, β-scission, small radicals addition (e.g. H• or CH_3•), substitutive addition of radicals onto unsaturated molecules (or displacement), dehydrogenation and demethylation, termination. The kinetic modelling has taken advantage of the previous experience in the fields of gas phase pyrolysis, like steam cracking for olefins production and, more recently, in that of liquid phase pyrolysis, like visbreaking. The kinetic constants of all the reactions classes have been derived from the equivalent ones of a hypothetical equivalent gas phase. Proper modifications have been applied to the activation entropies and energies, for their transposition into the condensed state (Benson 1960, Dente et al., 1997). The attention will be here focused on the peculiar aspect of delayed coking modelling that is the characterisation of the kinetic of substitutive addition reactions (the other reaction classes have been previously described by Dente et al., 1997, Bozzano et al., 2004).

The reduction of real components into an adequate number of pseudocomponents by means of lumping techniques (Clymans and Froment, 1984, Hillewaert et al., 1988, Ranzi et al., 2001) is mandatory. In facts, as said before, the high residence time of the accumulating condensed phase into the drum, leads to the polymerisation of the heavy poly-aromatic molecules, due to substitutive addition reactions (practically absent in the case of visbreaking). Consequently the kinetic scheme rapidly “explodes” into a great number of reactions. Initially a kinetic scheme of about 1600 equivalent reactions involving 450 equivalent components was prepared (visbreaking model consists in about 370 reactions involving 400 pseudocomponents). In a second time the reactions has been reduced to about 700 because after about 30 minutes the alkyl side chains of aromatics molecules are practically disappeared. Then the mentioned reactions essentially take place between methylated aromatic molecules and addition, dehydrogenation and demethylation reactions become predominant. Six groups of pseudocomponents represent the aromatics classes: 1) original aromatics, 2) aromatics resulting from the radicals attacks (and decomposition) on the side chain of original aromatics, 3,4,5) products of the substitutive addition of aromatic radicals on aromatic molecules (having from two to four poly-aromatic sheets connected by methylenic bridges), 6) coke precursors giving place essentially to dehydrogenation and demethylation. Once defined the methyls number, fused aromatic carbon atoms, hydrogen content of the new equivalent components, all the other properties, like specific heat, enthalpy of formation, boiling point, specific gravity and so on, can be derived by means of group contribution methods reported into the literature (see for instance Benson 1976) or specifically developed.

Substitutive addition reactions are exemplified in Figure 2 (involving aromatic classes 3,4, and 5), where the addition of a large polyaromatic radical on an alkylated position of another aromatic sheet is presented:

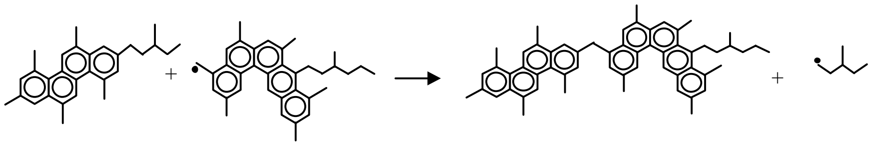

Figure 2. Example of substitutive addition reaction

The substitutive addition on the position where side chain is present is quite more favoured, and justify, together β-scission, the fast reduction of the concentration alkylated aromatic structures in favour of that of methylated ones. The produced paraffinic radical abstracts hydrogen on the substrate forming methane (in case of attack on a methylated position) or a paraffin. The very low concentration of four polyaromatic sheets in the multiple sheets structures produce negligible further addition reactions so that they have been assumed as the larger possible aromatic molecules. Moreover their geometrical configuration creates such sterical hindrance to drastically reduce the efficiency of interactions with other large poly-aromatic radicals. The heavy components (aromatic class 6) can dehydrogenate or demethylate giving place more and more to coke precursors (Figure 3).

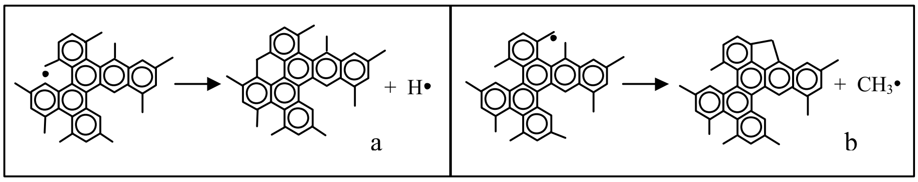

Figure 3. Examples of dehydrogenation(a) and demethylation(b)of polyaromatic radicals

The H/C ratio of the residing product, defined as "coke", gradually decline (final ratio is in the range of 0.5-0.7) and significant amount of methane is detected in the effluents. The liquid phase becomes more and more viscous so that the termination reactions are progressively slowed down. This results in the increase of polyaromatic radicals concentration with time, producing a sort of global vapour production rate uniformity. Of course the production of light fractions changes in favour of more gases at the expense of the other distillates (gasoline and gasoils decrease at high residence times after achieving a maximum). The described mechanism is supported by some experimental data related to kinetic studies of coke production (A. Del Bianco *et al.*, 1993). The typical substitutive addition kinetic constants used in the delayed coking model are: $k_{ADD} = 10^{8.7}$ exp(-24000/RT) [m^3/kmol/s] for each alkylated position and $k_{ADD} = 10^{8.7}$ exp(-26000/RT) [m^3/kmol/s] for each methylated position, while for dehydrogenation k = 10^{15}exp(-37000/RT) (Figure 3a) and for demethylation k = $10^{12.75}$exp(-29800/RT) (Figure 3b).

3. Reactor modelling

The furnace modelling (fouling rates included) has been performed on the same conceptual bases already verified and tuned for the visbreaking process. The mathematical description of the phenomena occurring in the drum is more complex to be faced on. The presence of at least two phases and the fact that only one, the vapour, leaves the reactor (semi-batch), makes more difficult the resolution of the equation system; furthermore the modelling is complicated by the large number of pseudo-components and reactions. The lighter products in some cases are in supercritical conditions, while the heavier ones, again subject to evaporation, present an equilibrium partition between the two phases. Moreover a third phase (the so called mesophase) progressively grows as a dispersed precipitate, mainly constituted by the heaviest poly-aromatics cata- and peri-condensed components. The mesophase is not participating to vapour-liquid equilibrium. Thermodinamic properties like vapour pressure, heats of vaporisation, and so on, have been derived by using conventional rules. The composition of the liquid (and solid) phase in the drum (and in the outlet vapour stream), the flow rate of the effluent and the drum average temperature are deduced by integration of the mass and enthalpy balances, together with ideal equilibrium assumption, given the pressure at the exit of the drum.

4. Results and Comparisons

The model ability in predicting products yields and properties has been verified by comparison (Table 2) with commercial plant data for five different feedstocks, covering a sufficient large range (Table 1) and referred to different gasoil recycle ratios.

Table 1: Properties of the five feedstocks simulated

	1	2	3	4	5
Residue type	atm.	atm.	vac.	atm.	vac.
Sp. gr. 15°/4° g/cm^3	0.998	1.044	1.065	0.98	1.026
S wt%	4.83	8.3	8.8	3.3	4.0
CCR	9.1	17	20	14	20
Viscosity Cst (50°C)	30	400.000	25.000.000	1100	400.000

The obtained results seem to confirm the validity of the model.

Table 2: Comparisons among experimental data and simulations

Products wt%	**1**		**2**		**3**		**4**		**5**	
Gasoil recycle (% feed)	0		6		15		6		15	
	Exp.	Theo.	Exp	Theo.	Exp.	Theo.	Exp	Theo.	Exp	Theo.
Gas (≤ C_4)	6.72	6.9	9.6	9.2	11.3	10.7	6.6	7.0	9.0	8.5
L. Gasoline (C_5-80 °C)	2.91	2.94	4.6	4.4	4.2	4.6	4.8	4.3	4.2	4.4
H. Gasoline (80-180°C)	10.6	10.5	7.5	8.0	6.8	7.0	7.9	8.1	6.8	7.0
Sp. G. 15°/4° g/cm^3	0.777	0.775	0.76	0.77	0.76	0.76	0.75	0.76	0.75	0.75
S wt%	2.1	1.5	3.0	3.2	3.3	3.1	1.2	1.3	1.5	1.3
L. Gasoil (180-350°C)	31.8	31.9	27.7	29.0	24.0	26.4	32.5	32.4	26.2	26.1
Sp.G. 15°/4° g/cm^3	0.90	0.91	0.88	0.87	0.88	0.86	0.86	0.85	0.86	0.85
S wt%	3.0	2.6	4.3	4.5	4.8	4.1	2.0	1.9	2.5	1.9
H. Gasoil (>350 °C)	30.1	30.5	24.4	23.8	22.8	22.4	26.1	26.7	22.8	22.7
Sp.G. 15°/4° g/cm^3	0.96	0.96	0.96	0.97	0.96	0.97	0.94	0.94	0.94	0.95
S wt%	3.3	3.0	4.5	5.0	5.0	4.8	2.6	2.2	3.0	2.2
Coke	17.8	17.7	25.5	25.4	30.2	28.9	21.4	21.5	30.3	31.3
S wt%	6.1	5.95	8.0	9.0	10.0	9.5	3.3	3.7	3.3	3.8
H_2S	1.4	1.56	3.4	3.1	3.9	3.7	1.3	1.1	1.6	1.5
$CH_4 + H_2 + C_2^{\pm}$	3.0	3.31	3.7	2.4	4.3	2.8	3.1	2.2	4.3	2.8
$C_3^{\pm}$	1.4	1.0	1.1	1.2	1.4	1.3	1.0	1.1	1.4	1.3
$C_4^{\pm}$ *	1.0	1.5	1.4	2.6	1.7	2.9	1.2	2.4	1.7	2.9

* (in the industrial cases part of the C_4 are entering into the light gasoline fraction)

For emphasizing the model flexibility, also some kinetic data, derived from a batch microreactor in a wide range of temperatures and residence times (A. Del Bianco et al., 1993), have been evaluated. The adopted feed is a Belaym vacuum residue with the following properties: specific gravity 15/4: 1.028 (g/cm^3), kinematic viscosity at 100 °C: 5230 Cst, CCR (wt%): 20.8, asphaltenes (wt%) 18.6. The comparison among experimental distillate yields and the predictions of the model is shown in Figure 4. The maximum observed in the yields depends on the rising with time of the partial pressure of the distillates rising with the time in the batch unit, so that partial condensation of the heavy fractions takes place. This phenomenon is responsible of the gasoline and gas increase at the expense of heavy gasoil.

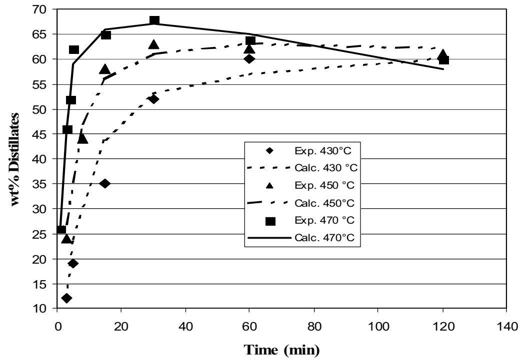

Figure 4. Comparison among simulations and experimental data of a batch microreactor

5. Conclusions

The basic concepts adopted in the modelling of Delayed Coking process have been exposed. The preliminary results, both in terms of yields properties of effluent fractions, seem to be in good agreement with the available experimental data. The possibility of predicting the coke quality is still under consideration.

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