KINETIC MODELING AND HYDROCARBON MIXTURE PROPERTIES CHARACTERISATION IN COKING OPERATIONS

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Refinery thermal processes are diffused all over the world, because of their relatively simple configuration and operating flexibility compared to catalytic processes. In particular Delayed Coking is coherent with the growing demand for transportation fuels, more stringent legislation and the opportunity for significant improvement in refinery profit margins. The coking capacity has in fact increased by about 50 million tons from 1999 to 2005 (Valyavin et al., 2007). The development of extended kinetic models can help to accurately describe these processes (characterised by liquid phase pyrolysis) and can be useful for their better description. Such modeling tools are also convenient supports for the production planning, the optimisation of the process and the operator training. This paper present a detailed, mechanistic model of Delayed Coking process and some results compared with experimental data. Moreover a first approach to fluid- and flexicoking modeling is presented.

1. INTRODUCTION

Delayed coking is a cyclic process that thermally cracks vacuum residue or other residue feedstocks to upgrade and convert petroleum residua (atmospheric and vacuum distillation residues of crude, but also other refinery streams) into liquid and gas product streams; petroleum coke (PET coke) is the solid heavy tail of the process. It is a key technology for residue upgrading and no fuel oil production. While this is a mature technology, improvements in key areas such as operability, safety and reliability can be still obtained. The main advantages for adopting this process can be resumed as follows: refineries can use heavier, cheaper crudes to increase margins converting low-value residues to high-value fuels with moderate capital investment, easy integration into existing refinery, safe, reliable and well-proven technology. The typical Delayed Coking Unit (DCU) is constituted by a furnace followed by a semibatch adiabatic reactor called "coking drum" (see figure 1). A recycle stream of gasoil is frequently adopted in order to increase the amount of vaporisation, so reducing the residence time in the furnace and improving the heat transfer coefficient into the coils. The fired heater has horizontal tubes and reaches final temperatures of 485 to 505°C. Short residence times are adopted in the furnace tubes, the final coking is thereby "delayed" to the coking drum downstream of the heater. The precursors of the mesophase formation (and therefore of the final coke) gradually fill the reactor drum (as far as 60-70% of its volume); the vapour produced in the furnace, and in the drums, exits from the top. A main channel is formed similar to the trunk of a tree (figure 2). As time goes on, the liquid pool above the solid decreases and the liquid turns to a more viscous type tar. This tar flows back down towards the main channel which can solidify at the top forcing the channel to branch. So the limbs of the "tree in the drum" start to appear. This proceeds up through the coke drum. Sponge coke, which includes needle coke, is formed from this liquid which remains in a relatively quiescent zone among the main branches or channels, up through the coker. Shot coke has a different type of coke structure showing that it is mainly produced while suspended in the vapor phase in the drum. The physical structures and chemical properties of the PET coke determine its end use: it can be burned as fuel, calcined for use in the aluminum, chemical, or steel industries, or gasified to produce steam, electricity, or gas feedstocks for the petrochemicals industry.
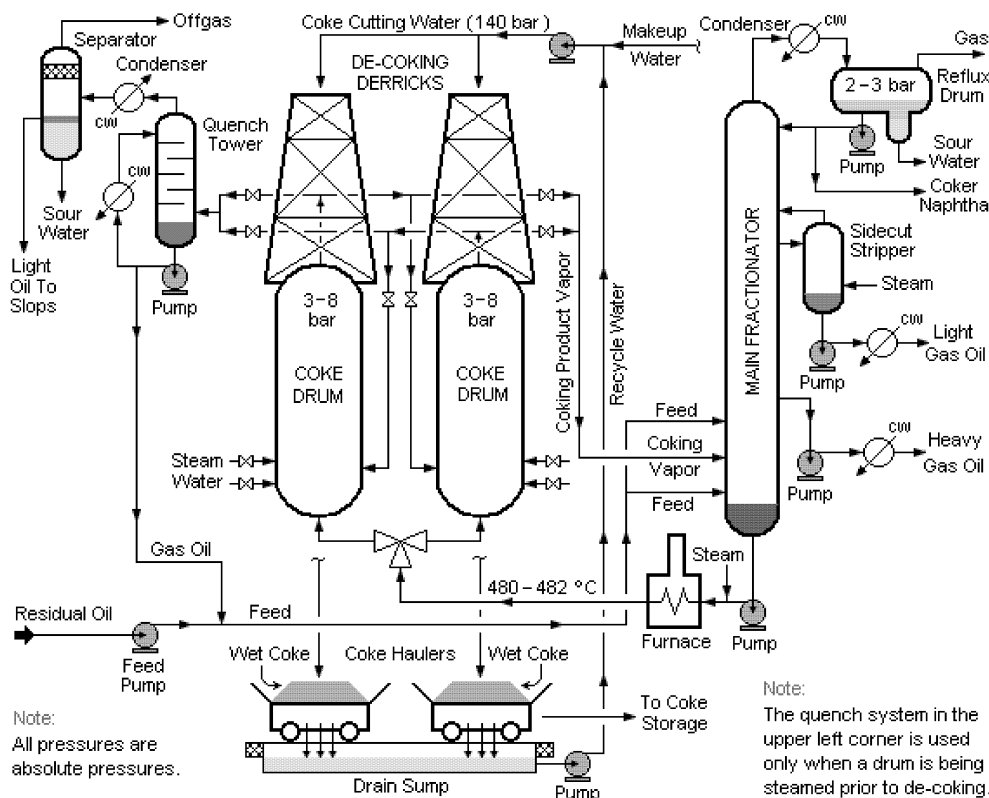
Fig. 1: Schematic configuration of a DCU

The feed stream is periodically switched between drums with time intervals depending on the feed rate, drum size, and throughput capacity. Delayed cokers currently have cycle times from 12 to 24 hours, with one drum filling on-line while its counterpart is off-line for stripping, cooling, and solid recovery. Shortening the cycle time is one method of increasing throughput on DCU, but it is extremely difficult due to time requirements for each of the steps of the drum cycle.

In the past some attention has been given to the kinetics and reactor modeling of DCU. Only macroscopic or regression models was presented (Takatzuka et al., 1989, Wiehe, 1993, Del Bianco et al., 1993, Rahmani et al., 2002, Chen and Wang, 2010). A detailed approach to the description of the process, consisting of a kinetic scheme of about 750 reactions involving 470 pseudocomponents is here presented. Compared with the usual empirical macro-kinetics approach, this kind of model allows a wide generalization over the different kind of feedstocks and a large range of extrapolation for different operating conditions. The model includes also the characterization of hydrocarbon mixture and products properties like specific gravity, viscosity, sulphur content, boiling points and so on.

2. LUMPING OF COMPONENTS

The complexity of the molecular composition of the HC residues and pyrolytic products has been reduced by lumping the "infinite" number of real components into a relatively limited number of pseudo-components (Dente and Ranzi, 1983; Jacob *et al.*, 1976; Vynckier and Froment, 1991; Quann and Jaffe; 1992, Ranzi *et al.*, 2001). The "virgin" hydrocarbon mixture can be represented in terms of three macro-classes of components: alkanes, aromatics and naphthenes. Their pyrolysis gives place to unsaturated species: olefines, diolefines, cyclo-olefines

(with unsaturation on the alkylic chain or on the rings), aromatic olefins etc.. New polyaromatic species are also generated by substitutive addition reaction, progressively leading to the mesophase formation.
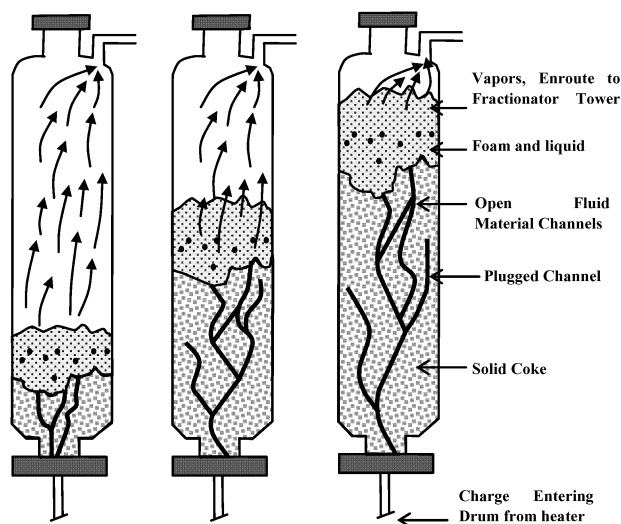

Figure 2: Schematic representation of coking drum during filling

All the real components contained into the lump react practically in a similar way, so that their internal distribution (and that of their products) remains almost unchanged along the reactions path. Thus, all the isomers can be conveniently grouped into a single lumped component both in the case of reactants and products. For instance, a large number of alkene isomers are formed during the pyrolysis of heavy alkanes. In order to avoid an excessive number of species, all these isomers are conveniently grouped and considered as a single lumped pseudocomponent. The same concept applies to the other macroclasses (like aromatics, naphthenes and so on).
In addition to this "horizontal" lumping among species with the same molecular weight, another very convenient simplification is adopted: the lumping of homologous species with a adjacent number of carbon atoms ("vertical lumping"). The "vertical lumping" is performed by using a linear distribution inside the interval.
In the case of residues here considered (and except for the products having less then 5 carbon atoms), it has been found convenient to lump the species covering an interval of -2,+2 C atoms with respect the number of carbon atoms of the center of the lump; a larger lumping interval, increasing with molecular weight, has been adopted for species with more the 65 C atoms (in facts with the increasing of molecular weight the detailed description of components becomes less and less important). Resuming, lumped components assemble in sections of 5 to 10 carbon atoms, while only few pseudo components are assumed to represent the heavier fractions. For example, an alkane lump with 23 C atoms represents all the paraffines (n- and iso-) from 21 to 25 carbon atoms. Alkane and alkene species are assumed to have preferentially a poly-isoprenoid structure (except in the proximity of the olefinic group): for paraffines it means that every four C atoms of the backbone a side methyl group is present. For cyclic species like naphthenes and aromatics a double statistic is assumed: at a fixed number of C atom a cyclic component can have a repartition among rings and side chains spanning from 1 ring to a maximum related to the number of C atoms. In order to represent these components experimental data on their characteristics have been analyzed (Ali et al., 1985) and it has been deduced that the catacondensed structure is the more favored. It has been assumed a methylation degree on the boundary of the polycyclic sheets equal to 0.5 and a single side chain having the same characteristics as alkanes. The internal distribution of aromatic rings has been recently assumed to have the same probability so that, for instance, an aromatic species having 23 carbon atoms represents, all the components reported into the following figure 3 with the same probability of occurrence.
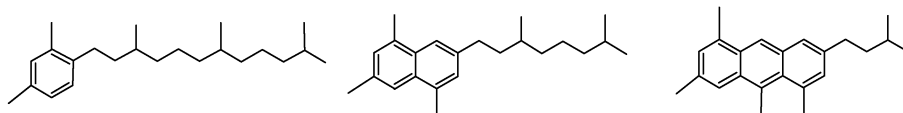
Figure 3: internal distribution of aromatic species

The maximum number of rings ($n_{ringmax}$), with the assumed geometry and a total number of C atoms n_c, results to be:

$$n_{ring\,max} = (n_c - 4)/5 \qquad (1)$$

By adopting this statistics all the properties in term of average length of side chain (C_{alk}), average number of C atoms into the aromatic ring ($C_{R,aro}$), average number of methyls (C_{met}) on the aromatic sheet boundary, average number of fused aromatic carbons (C_{fused}), can be deduced:

$$C_{alk} = 0.5 \cdot C_{aro} - 3.5 \qquad (2)$$

$$C_{R,aro} = 2.4 + 0.4 \cdot C_{aro} \qquad (3)$$

$$C_{met} = C_{aro} - C_{alk} - C_{R,aro} \qquad (4)$$

$$C_{fused} = 0.2 \cdot C_{aro} - 1.8 \qquad (5)$$

In the case of naphthenes the internal distribution of rings favors a reduced number of rings and longer side chains. By adopting analogous rules the "geometrical" properties of all these kind of components can be deduced.

3. FEED CHARACTERIZATION

As previously mentioned, feedstocks are usually made up of complex hydrocarbon mixtures derived from the refinery distillation residues (atmospheric or vacuum). For these feed PIONA and H/C can be estimated only through the analytical means (such as NMR) that are not usually available in refineries. Moreover, their final boiling point is not defined and the internal distribution of the different hydrocarbon classes of alkanes, cyclo-alkanes and aromatics has to be deduced in a different way. Inside each of these macro-classes, the relative amount of the components can be derived from the following statistical distribution (already reported in Bozzano et al, 1998):

$$\frac{df}{dn_c} = \frac{1}{n_{c,av} - n_{c,min}} \exp\left[-\frac{n_c - n_{c,min}}{n_{c,av} - n_{c,min}} \right] \qquad (6)$$

where f is the fraction of the components with n_c C atoms, $n_{c,av}$ and $n_{c,min}$ are the average and the minimum number of C atoms, respectively. This statistical distribution, which is also useful for heavy gasoils, was obtained after careful analysis and processing of some data available in the literature (Ali et al., 1985).

Only few experimental data are usually available to define the feed characteristics: initial atmospheric equivalent boiling point (AEBPI), kinematic viscosity, specific gravity, sulphur content and CCR (Conradson

Carbon Residue). AEBPI defines $n_{c,min}$ and the viscosity of the residue $n_{c,av}$. Specific gravity and CCR are essential to defining the relative fraction of the three hydrocarbon classes. Sulphur content is used for correcting the effective specific gravity of the hydrocarbon fraction. The specific gravity (SG) of different hydrocarbon classes is defined by means of group contribution methods especially developed. The following equations report the adopted relations:

$$SG_{alk} = 0.86 \cdot \frac{0.856 + 0.072\, H_{alk}/C_{alk}}{\left(1 + 1.144/C_{alk}\right) \cdot \left(1 + 0.71 \cdot C_{alk}\right)} \tag{7}$$

$$SG_{naph} = 0.86 \cdot \frac{0.856 + 0.072\, H_{naph}/C_{naph}}{\left(1 + 1.144/C_{naph}\right) \cdot \phi_{naph}} \tag{8}$$

$$\text{with: } \phi_{naph} = 1 + \frac{0.67}{C_{nafh}} - \frac{0.2121 + 0.55 \cdot F_{fused} - 0.3 \cdot F_{sub}\left(1 - F_{sub}\right) + 0.006 + 0.1\left(C_{naph} - C_R - 1\right)/C_{naph}}{C_{naph}} \cdot C_R$$

$$F_{fused} = \frac{4 \cdot C_R - 22}{7 \cdot C_R} \qquad F_{sub} = \frac{1.5 \cdot C_R + 11}{7 \cdot C_R}$$

$$SG_{aro} = 0.86 \cdot \frac{0.856 + 0.072\, H_{aro}/C_{aro}}{\left(1 + 1.144/C_{aro}\right) \cdot \phi_{aro}} \tag{9}$$

$$\text{with: } \phi_{aro} = 1 + \frac{0.71}{C_{aro}} - \frac{0.3554 + 0.32 \cdot F_{fused,aro} + 0.04 \cdot F_{sub,aro} + 0.032\left(C_{aro} - C_{R,aro} - 1\right)/C_{aro}}{C_{aro}} \cdot C_{R,aro}$$

$$F_{fused,aro} = \frac{2 \cdot \left(C_{aro} - C_{alk}\right) - 16}{4 \cdot \left(C_{aro} - C_{alk}\right) - 2} \qquad F_{sub} = \frac{C_{aro} - C_{alk} + 7}{4 \cdot \left(C_{aro} - C_{alk}\right) - 2}$$

F_{fused}, refers to the fraction of fused C atoms with respect of the total C atoms of the polyciclic structure (aromatic of naphthenic), F_{sub}, is the substituted one. H, is the number of hydrogen atoms, C the number of carbon atoms. C_R is the number of C atoms constituting the rings (naphthenic or aromatic). ϕ is a function of the polycyclic structure of the molecule.

4. KINETIC MODELLING

Of course the condensed phase pyrolysis follows the typical radical chain mechanism: initiations reaction, hydrogen abstraction reactions, β-scission reactions, addition reactions of small radicals (e.g. H• or CH₃•), substitutive addition of radicals onto unsaturated molecules (or displacement reactions), isomerisation, dehydrogenation and demethylation reactions, termination reactions. Because of the sterical hindrance, molecular rotation of large C-C segments are substantially inhibited and internal isomerization reactions of alkyl radicals can be neglected, at least for the evaluation of the overall degradation process.

Part of the rules and criteria adopted facing on the problem of the kinetic modeling of the liquid-phase pyrolysis of oil distillation residues present strong analogies with the ones already adopted in gas-phase pyrolysis kinetic schemes (Dente and Ranzi, 1983, Hillewaert *et al.* 1988, Dente *et al.* 1997, Bozzano *et al.* 2005). When the same reaction is "moved" from the gas to the liquid phase, in principle frequency factor and activation energy need to be modified, because of the condensed state. In facts entropy and enthalpy of the transition state change in passing from the gas to the liquid phase. The transposition to the liquid phase of rate constants can be evaluated (Benson, 1960) from:

$$\frac{k_{liq}}{k_{gas}} = \exp\left(\frac{\Delta S_{liq}^{\#} - \Delta S_{gas}^{\#}}{R}\right) \exp\left(-\frac{\Delta H_{liq}^{\#} - \Delta H_{gas}^{\#}}{RT}\right) \tag{10}$$

where: $\Delta S^{\#}_{liq} - \Delta S^{\#}_{gas}$ = entropy variation of the transition state in passing from liquid to gas phase (this variation is typically negative)

$\Delta H^{\#}_{liq} - \Delta H^{\#}_{gas}$ = enthalpy variation of the transition state in passing from liquid to gas phase (it is typically negative and about equivalent to an hypothetical heat of evaporation of the transition state)

The corrections can be significant essentially if the absolute value of reaction energy is very large, therefore they affect mainly initiation reaction and radical recombinations.

Lets start with some considerations regarding initiation reactions. Unlike in the case of gas phase, the change of entropy is related to the fact that, when the two radicals are formed they remains "caged" and cannot develop totally their translational and external rotational degrees of freedom (internal rotations and vibrational frequencies substantially remain the same in the reactant and in the transition state).

Just to give few examples, some initiation reactions related to C-C bond cleavage in heavy hydrocarbon and/or polymer decomposition in the liquid phase are reported (consequent to the application of the rule of simulating a fictitious condensation of the transition state).

Primary-Primary Carbon bond cleavage:

$$k = 10^{14.9} \exp\left[\frac{-41300 + corr(n_c)}{T}\right] \qquad —C \overset{\frown}{\rightarrow} C— \qquad [s^{-1}] \qquad (11)$$

Secondary-Primary Carbon bond cleavage:

$$k = 10^{14.9} \exp\left[\frac{-40500 + corr(n_c)}{T}\right] \qquad \begin{matrix} & C & \\ & | & \\ —C & \overset{\frown}{\rightarrow} C— & \end{matrix} \qquad [s^{-1}] \qquad (12)$$

Allyl (or Allyl-like and Benzyl-like)- Primary Carbon bond cleavage:

$$k = 10^{13.5} \exp\left[\frac{-36000 + corr(n_c)}{T}\right] \qquad —C = C — C \overset{\frown}{\rightarrow} C— \qquad [s^{-1}] \qquad (13)$$

having defined the function $corr(n_c) = 575\sqrt{200 \cdot n_c / (200 + n_c)}$, where n_c is the number of carbon atoms of the heavy component or simply the number of carbon atoms characterising the so called flow unit (Van Krevelen, 1976) for the diffusion in the molten polymer.

Propagation reactions rate constants can be evaluated as in the case of gas phase because the "caging effect" previously mentioned is negligible (Ranzi et al., 2001). H abstraction on the pseudo-components is followed only by the resulting radical kinetic competition among their H re-abstraction (on the neighbouring hydrogen of other molecules) and their β-scission (that produces smaller pseudo-components and radicals). However the related activation energies, typical of H-abstraction reactions, together with the high concentration of neighbouring H atoms in the liquid phase, make the H re-abstractions extremely faster than the β-scission rates. Therefore these latter constitute the rate determining step of the decomposition. Of course, the (smaller) radicals produced through those β-scissions, quasi-immediately generate the equivalent molecules before undergoing a new β-scission.

Among propagation reactions, in Delayed Coking process, particularly important are substitutive-addition reactions, in relation to the high residence time inside the drum. In facts they are the responsible of mesophase

generation leading to coke formation after de-hydrogenation, de-alkylation and de-methylation of "aromatic polymers" produced by addition reactions. This latter class of reactions involves alkylated polyaromatic molecules; it consists of addition of highly resonant aromatic radicals (i.e. benzyl-like) to the alkyl-substituted positions of the aromatics rings, followed by the expulsion of the alkyl radical (e.g. CH_3) and consequently the substitution of those (paraffinic) groups with aromatic structures. This mechanism is similar to a radicalic polymerisation process generating high molecular weight structures.

The lumping into equivalent reactions is even more important in the case of delayed coking, with respect to other thermal treatments (like, for instance, to visbreaking) being typically characterized by second order reactions. In absence of the convenient lumping rules, the kinetic scheme could rapidly "explode" into a huge number of reactions. Five 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, see the qualitative figure 4). The nature of the substitutive addition reactions is exemplified in Figure 5, where an addition of a large polyaromatic radical on an alkylated position of another aromatic sheet is presented. In the range of temperature of interest for delayed coking process, the substitutive addition on the position where alkyl side chain is present is quite more favored compared to the positions where methyl or aromatic hydrogen are present. However it is worth of mention that roughly after about half an hour in the drum, the estimated average size of the polyaromatic side alkyl chains is so drastically reduced, that addition on methylated and hydrogenated positions, dehydrogenation and demethylation reactions become predominant. Therefore substitutive addition on alkylated positions can be neglected. The typical substitutive addition kinetic constants used in the delayed coking model are consequently:

For each methylated position

$$k_{add} = 10^{8.7} \exp\left(-\frac{26000}{RT}\right) \qquad\qquad [m^3/kmole/s] \qquad\qquad (14)$$

for each aromatic hydrogen position (Car-H)

$$k_{add} = 10^{8.7} \exp\left(-\frac{28000}{RT}\right) \qquad\qquad [m^3/kmole/s] \qquad\qquad (15)$$

The produced paraffinic radical abstracts hydrogen on the substrate forming a paraffin or methane (in case of attack on a methylated position), or hydrogen (after attack on Car-H position). An approximately maximum number of four polyaromatic sheets in the multiple different sheets structures can be justified. In fact the resulting concentration of these last oligomers is anyway very low (because they come out from three subsequent acts of substitutive addition) so that further addition reactions are negligible. Moreover the generated geometrical structure (see figure 4c) creates such a sterical hindrance to drastically reduce the efficiency of interactions with other large poly-aromatic radicals.
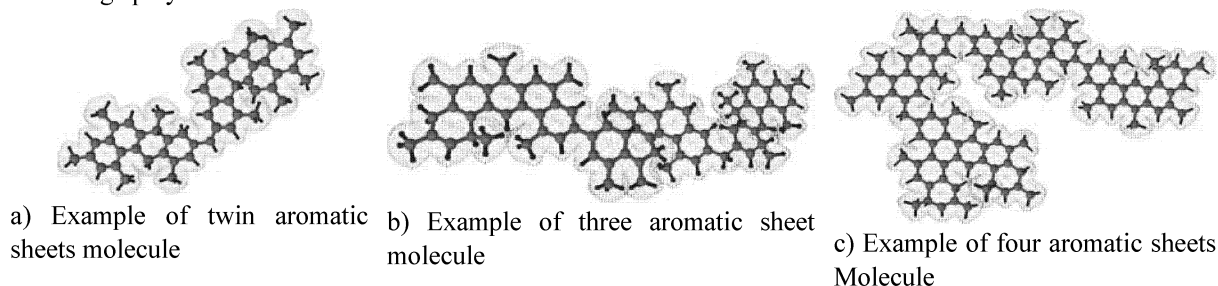

a) Example of twin aromatic sheets molecule

b) Example of three aromatic sheet molecule

c) Example of four aromatic sheets Molecule

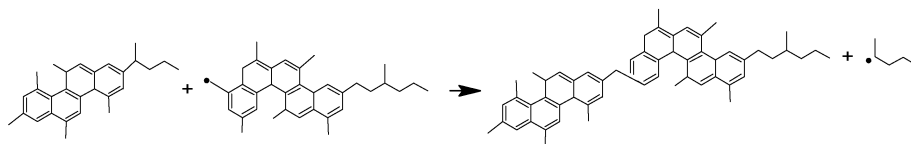*Figure 4: examples of poly-condensed aromatic molecules*

Figure 5: Example of substitutive addition reaction generating a twin aromatic sheets component

These high molecular weight structures can then internally dehydrogenate or demethylate, more and more giving place to the coke precursors (Figure 6). The typical kinetic constant for these internal de-hydrogenation and de-methylations is:

$$k_{add} = 10^{12.8} \exp\left(-\frac{30000}{RT}\right) \qquad [m^3/kmole/s] \qquad (16)$$

The polymerisation mechanisms, coupled with progressive de-alkylation and de-hydrogenation justify the progressively lower hydrogen content of the drum residing product, defined as "coke" and the presence of a significant amount of methane in the effluents. The H/C ratio of the residing product, i.e. the liquid hydrocarbon reacting mixture containing the dispersed mesophase becoming "coke" at the end of the treatment, gradually decline (final ratio is in the range of 0.4-0.6) and significant amounts of methane and hydrogen are detected in the effluents. The liquid containing the dispersed mesophase becomes more and more viscous so that the termination reactions become more and more difficult. The consequence is the rising with time of polyaromatic radicals concentration. Then the last phenomenon is responsible of a sort of global vapour production rate uniformity along the time. 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). Apart from the qualitative considerations, the described mechanism is supported by some experimental data related to kinetic studies of residue degradation (A. Del Bianco et al., 1993).

The definition of radicals concentration has been deduced by adopting a continuously varying steady state approach. The relatively low maximum process temperature level ($\leq 500°C$), suggests that practically no significant reaction can take place into the vapour phase.

Finally lets discuss about the other special class of reactions into the condensed phase, represented by termination reactions. In this case it is convenient to make use of the collision theory, with an orientation factor, for deducing the kinetic constants. When radicals are approaching, with the proper orientation, in the condensed phase, they recombination is so fast that, inevitably, their mobility is reduced: therefore the radical recombination is diffusively limited. The number of collisions per unit volume and time among radicals have been evaluated from Benson (1960) and it is given by: $4\pi \cdot r_A \mathcal{D}_{AS} C_{AS}$ (where r_A is the distance among the atoms containing the radical positions, typical C-atoms, $\mathcal{D}_{AS}$ is the diffusion coefficient of the radical in the surrounding, C_{AS} is the radical concentration in the surrounding).
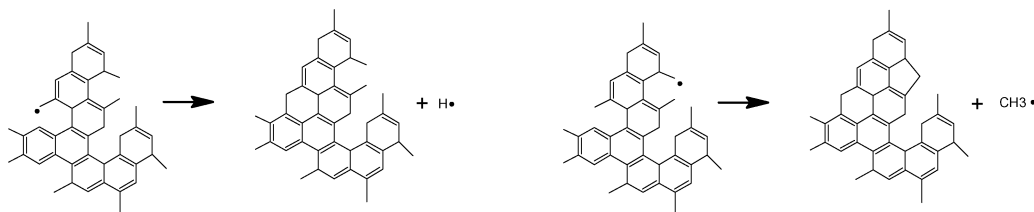

Figure 6: Examples of internal dehydrogenation and demethylation of polyaromatic radicals

The previous expression represents the number of collisions for the single radical A. By multiplying for the number of molecules per unit volume, the number of collisions referred to the unit volume is obtained (N_{AV} = Avogadro number). So the "kinetics" of collision is given by:

$$v_{coll.} = \frac{4\pi r_A}{2} \mathcal{D}_{AS} \left(\frac{N_{av}}{1000} \right) C_{AS}^2 = k_{coll} C_{AS}^2 \tag{17}$$

The ½ factor is to avoid counting the collisions 2 times. k_{coll}, is the equivalent the collision constant [m^3/kmole/s]. The fraction of collision with orientation favourable to the coupling is the same as in the gas phase. The self-recombination constant is therefore given by:

$$k_{AA} = k_{coll} \cdot \Phi_{AA}^2 \tag{18}$$

where Φ_{AA}^2 is the orientation factor of the collision necessary for making effective the recombination: it is evaluated as in the case of gas phase. For the recombinations A-B the traditional simmetry rule is valid:

$$k_{AB} = 2\sqrt{k_{AA} \cdot k_{BB}} \tag{19}$$

This rule has the obvious advantage of drastically reducing the number of useful recombination constants simply reported to the evaluation of the self-recombinations. The k_{coll} evaluation deserves some further consideration. First of all, the Stokes-Einstein theory suggests that, at least when molecules are not too "long" (the exclusion regards the case of polymers or that one of solvents with extended linear backbones):

$$\mathcal{D}_{AS} \cong \frac{kT}{3\pi\mu_S r_A} \tag{20}$$

where, k, Boltzmann constant; μ_S, liquid viscosity; T, absolute temperature. The viscosity μ_S can be estimated with sufficient accuracy (according to the Eyring theory), by the expression:

$$\mu_S \cong \frac{N_{Av} h}{\tilde{V}_S} \exp\left(\frac{E_v}{RT} \right) \tag{21}$$

where: h, Planck constant, $\tilde{V}_S$, molar volume of the liquid or of the polymer segment = PM_S/ρ_S (PM_S, average molecular weight of the liquid; ρ_S , liquid density); E_v, energy required for the viscous motions. It can be approximately estimated as $E_v \approx 0.36 \, \Delta H_{ev}$ where ΔH_{ev} is the heat of vaporisation of the liquid at the normal boiling point. When ΔH_{ev} is not available, the simple Trouton rule $\Delta H_{ev} \approx 21 \, T_b$ can be applied (T_b, absolute temperature of liquid normal boiling point). For a given number of carbon atoms the atmospheric equivalent boiling point can be deduced by the following expressions proposed by Altgelt and Boduszynski (1994):

$$MW_{AEBP>500F} = 140 + 3.40x10^{-7} \frac{AEBP^3}{SG^{2.5}} \tag{22}$$

$$MW_{AEBP<500F} = MW_{AEBP>500F} \left[1 - 1.4x10^{-4} \left(600 - AEBP \right) \right]$$

In the case of molten polymers or oligomers, or of solvents characterised by highly extended linear backbones, the proposed expression is the same, but, as described by Van Krevelen (1976), E_v corresponds to the so called unit of flow energy, i.e. the energy needed for moving the proper segment of the chain in the viscous flow. The same concept is applied also to $\tilde{V}_s$, that becomes the molar volume of the "segment".

Therefore, by combining the given expressions, it follows:

$$k_{coll.} \approx 10^{10.2}\, T \cdot \tilde{V}_s \exp\left(-\frac{E_v}{RT}\right) \tag{23}$$

It is meaningful to observe that the self-recombination kinetic constant follows an Arrhenius-type formula where E_V assumes the role of activation energy.

5. REACTOR MODELLING

The modeling of the furnace (fouling rates included) has been performed on the same conceptual bases already verified and tuned for the visbreaking process (described in Dente *et al.*,1997). The mathematical description of the phenomena operative 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, makes hard 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. It is mainly constituted by the heaviest poly-aromatics catacondensed components precipitating after their aggregation. The mesophase can be excluded from the vapour-liquid equilibrium. In the present version of the model properties like the vapour pressure, heats of vaporisation, and so on, have been substantially deduced by using simplified and traditional rules like Clausius-Clapeyron, Trouton, Watson etc.. For supercritical components the vapour pressure is assumed equal to the critical one. The composition of the liquid (and solid) phase in the drum (and in the outlet vapour stream), the flowrate of the effluent and the drum average temperature are deduced by integration of the mass and enthalpy balances, together with the Raoult ideal equilibrium assumption, given the pressure at the exit of the drum. Thermodynamic properties of the pseudocomponents are built-up on the basis of group contribution methods.

6. RESULTS AND COMPARISONS

The ability of the model in predicting products yields and properties has been verified through the comparison (Table 2) with some data for six different feedstocks, covering a sufficient large range of properties (Table 1). Table 2 reports also the comparison of the properties of products in terms of specific gravity and sulfur content. The data are taken from Sawarkar et al. (2007) and refers to estimations at constant pressure and recycle ratio perfomed by DeBiase and Elliott, 1982)

Table 1: Properties of the six feedstocks simulated

	1	2	3	4	5	6
Residue	Brega	Orinoco	Alask. N. S.	Maya	Light Ar.	Heavy Ar.
TBP cut point, °C	565+	510+	565+	565+	565+	565+
Gravity, °API	12.3	2.6	8.9	2.6	7.4	4.5
S wt%	1.06	4.4	2.16	4.91	4.1	5.25
CCR	14.6	23.3	16.1	25.5	15.4	24.2

Table 2: Comparisons among data of DeBiase and Elliott, 1982 (Ref.), and simulations (Calc).

Products wt%	1		2		3		4		5		6	
	Ref.	Calc.	Ref.	Calc.	Ref.	Calc.	Ref.	Calc.	Ref.	Calc.	Ref.	Calc.
Gas ($\leq C_4$)	7.0	6.7	16.3	16.5	11.3	11.5	13.2	13.0	11.1	11.4	13.2	13.0
Naphtha (C5-193°C)	18.6	19.1	16.2	16.4	14.6	14.3	19.3	19.5	16.1	15.9	13.5	13.4
Gravity, °API	60.7	60.1	50.0	50.1	57.6	58.1	54.9	54.4	58.8	58.1	55.6	55.8
S wt%	0.11	0.12	1.25	1.26	0.7	0.69	0.9	0.89	1.0	1.02	1.1	1.2
Gasoil (193+°C)	52.4	52.0	29.6	29.8	47.6	47.0	29.2	28.9	45.8	46.2	40.4	40.7
Gravity, °API	35.7	35.0	18.8	19.1	25.1	25.5	20.9	21.3	28.1	27.7	26.5	26.1
S wt%	0.83	0.84	4.1	3.9	1.4	1.5	3.6	3.4	2.3	2.5	2.4	2.2
Coke	22.0	22.2	37.9	37.3	26.5	27.2	38.3	38.6	27.0	26.5	33.0	32.9
S wt%	1.9	1.8	4.3	4.2	3.0	3.1	5.6	5.8	6.4	6.2	7.1	7.0

The obtained results seem to confirm that the model is already very promising. Other comparisons are reported in a less extended paper (Bozzano and Dente, 2005) related to preliminary results of the modeling activity.

8. ESTENSION OF THE KINETIC MODEL TO OTHER COKING PROCESSES

Of course, due to the fundamental approach followed, the kinetic model cannot be considered limited to the delayed coking. Presently some preliminary estimations for the extension of the same kinetic model to the use in simulating fluid and flexi-coking processes have been performed. In these processes residence time differs from that of delayed coking (about 1h), however the temperature level is higher (from 625 to 480°C, with an average temperature of 550°C). The heated particles of coke enters into the chamber where they meet the dispersed feed at about 300°C. A very thin layer (of the order of 10^{-5} m) of oil is formed over the particles and reacts receiving the heat from the particles. The pyrolysis of the thin liquid gives place to the typical products, leaving a final coke layer, stratified over the original particle. When particles become too heavy to be fluidized they settle on the bottom of the reactor and then are transferred to the regenerator. The heating of the hydrocarbon film is practically instantaneous and can be considered at the same temperature of the surface of the particle. In some way liquid film behaves as a micro-reactor with the particle supporting it that is the batch heat reservoir. When adopted in fluid- and flexi-coking processes, the model can therefore give reliable results, and also about the same products will be obtained.

9. CONCLUSIONS

In this paper the fundamental concepts adopted in the modelling of Delayed Coking process have been exposed. The problem is made complicated by the huge number of components and reactions that are involved. Also the mechanisms leading to coke formation are not simple. The coking drum is described as a semi-batch adiabatic reactor. In this system the large number of species involved is interested both by physical equilibria and reactions into the condensed phase. The very minor role of the reactions in the vapour phase can be neglected.

The results reported in this paper, both in terms of yields and macroscopic properties of delayed coking effluents fractions, seem to be in good agreement with the available experimental data. The possibility of predicting the coke quality is still under consideration, together with the extension of the model to fluid- and flexi- coking processes. The outstanding advantage of this fundamental modeling is that no adaptive parameters are generally requested after the initial tuning with experimental data.

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