Pyrolysis Kinetics and Mechanism for Average Molecular Structures of Heavy Oil Crudes.

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ABSTRACT

A molecular kinetic model named PYRO2, for pyrolysis of heavy crude oils, has been developed. This model uses average molecular structures (AMS) derived from experimental analytical data obtained from heavy crude oils. The PYRO2 model consists of about 50 reactions associated with homolytic C-C, C-S, C-N and C-H bond breaking over saturated chains, bridges and cycles bounded to condensed rings. This model was applied to average molecules of Athabasca and Boscan crude oils in order to reproduce thermal conversion and product distribution data. The dependence of conversions to volatile products and coke yields on temperature and time of reaction are reproduced within a 10 % deviation from the experimental results. Variations in the distribution of gas and liquid components of volatile products follow the same tendencies as experimental results; but they depart significantly from the absolute values. This may indicate that new reaction paths and/or additional corrections in the AMS's are necessary. Two such factors, one of each, were identified..

INTRODUCTION

In very complex systems, like crude oils, the reaction mechanism and associated kinetics are not directly accessible for individual molecular entities. Kinetic models are thus based on different representations of molecular aggregations or the key properties of interest. According to the methodology used, kinetic models can be divided in three categories: (a) Pseudokinetic Models, in which the reaction schemes are associated with transformations of pseudocomponents that represent the crude oil fraction. Due to the fitting parameters they contain, their predictive capacity is limited to the specific crude oil and/or the process to which they were defined [1]. (b) Kinetics of model compounds, which use simple molecules to simulate reactions associated with substructures of very complex systems. These models assume similar behavior in the substructures they intend to represent [2]. (c) Kinetic models of complex systems, in which it is given explicit molecular structure of reactants and intermediates used to represent the crude oil or its components. The reactants can be represented by a distribution of individual molecules, stochastically generated by a Monte Carlo methodology, or by an average molecule [3-5]. In this work the kinetic model PYRO2 uses average molecular representations of crude oil. They were obtained based on elemental analysis, proton NMR and VPO molecular weights using a methodology described in the literature [6-9].

MODEL DEVELOPMENT

In its most simple form, it is possible to associate the pyrolysis process with homolytic C-X (X=C, S, N, H) bond scissions in the molecules R-R' of crude oil to produce two free radicals:

$$R - R' \rightarrow R. + R'. \qquad (1)$$

To start with, we builded up our kinetic model with the minimum set of elemental reactions necessary to produce results comparable with experimental data from our own work or from the literature. In future work, complexity will be increased as necessary according to the results of this comparison. Therefore the PYRO2 model only considers neutral molecules and does not contain the evolution of radical fragments. Accordingly, we assumed stabilization of the free radicals in reaction (1) with hydrogen from any internal hydrogen transfer mechanism and use the generalized reaction:

$$2H + R - R' \rightarrow RH + R'H \qquad (2)$$

where each bond breaks in R-R′ according to the Arrhenius expression of kinetic rate constant (k):

$$\ln(k) = \ln(A') + Ea/RT \qquad (3)$$

The pre-exponential factor A' was obtained from Gavalas et al. [10]. The activation energy Ea was calculated based on the Bell-Evans-Polanyi principle (BEP) [11,12]. This principle associates the change of energy between the reactants and the transition state (Ea) with the reaction enthalpy for a given elemental step in the kinetic mechanism. In our case the rate determining step depends on the difference in energy between the bond breaking step BS(C-X) and the bond formation step for RH and R'H, represented by a constant c. We found a practical way to evaluate the Ea parameter of (3) for reaction (2) for any C-X bond scission according to the expression:

$$Ea \sim BS(C\text{-}X) - c \qquad (4)$$

where c=49.40; 44.97; 49.40 for X=C, S, H and BS(C-X) are the C-X bond strengths.

We found a linear correlation between the experimental BS parameter and the theoretical quantum parameter known as Diatomic Energy (DE) for a series of very different compounds:

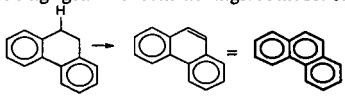
$$BS(A\text{-}B) = a + b\, DE(A\text{-}B) \qquad (5)$$

This equation allowed us to evaluate the BS parameter for any other compound or structure of interest. Correlation (5) was obtained as follows:
We selected simple model molecules whose BS parameters were tabulated in the CRC Handbook [13] and evaluated the Diatomic Energy (DE). The linear regression parameters a and b were then obtained. The Diatomic Energies (DE) were calculated using an energy partitioning scheme presented by Kollmar [14] for the analysis of *ab initio* and semi-empirical SCF calculations. The resulting value can be associated with the bond strength Ruette and Sanchez[15] have proposed this parameter as a tool for bond analysis. Based on semi-empirical methods, the following expression was obtained:

$$DE(A-B) = \sum_{i,j \in A,B} p_{ij}(h_{ij} + f_{ij}) \qquad (6)$$

Where h_{ij}, p_{ij} and f_{ij} are the one electron matrix, bond order matrix and Fock matrix elements, as obtained from the INDO1 calculations [16]. DE(A-B) contains contributions of the resonance energy and of the electron exchange energy to the bond and does not contain electrostatic energy terms which are included by the one-center energy terms. The second purpose of using the DE parameter is to establish an increasing order for Energy Dissociation of bonds in the reactant AMS of interest. We associated each bond breaking in the molecule to an elemental step in our kinetic model, obtaining schemes like that depicted in Table 1. Afterwards, we compared the theoretical products distribution with the experimental distribution derived from the pyrolysis. This allowed us (a) to check the practical consistency of the kinetic model, and, (b) to check the molecular structure proposed as model for the fractions here considered. Table 1 shows the parameters obtained from the best linear fit of the calculated ED (in Hartrees) to the experimental dissociation energy BS for C-C, C-S and C-H bonds.

Afterwards we introduced the following conditions in the kinetic model:
a) Hydroaromatic rings generate aromatic rings. A model of this type of reaction is:



(7)

The activation energy (Kcal/Mol) was defined as:

$$Ea = BS(C\text{-}H) - 166.92 - 23.8\, n \qquad (8)$$

where n is the number of aromatic rings generated in the reaction; in this case, n = 1. b) The sequence of bond breakings in each molecular structure was organized by increasing C-X bond energies from quantum mechanical calculations. c) The aromatic C-C, C-S and C-N bonds are not broken.

3. RESULTS

We applied the PYRO2 kinetic model to the pyrolysis of the AMS depicted by Cotte [17] for Boscan asphaltenes (Fig. 1) and Sanford [18] for Athabasca residue (Fig.2). The differential equations associated to the rate laws of the elementary reactions proposed in this study were solved using a Fortran program developed by Braum and coworkers [19]. Boscan asphaltenes pyrolysis can be represented by the cracking of the aliphatic side chains (some could be bridges) and naphtenic cycles. This process leaves the peri-condensed aromatic rings system as coke, represented by a black circle in the compact representation of Fig. 1. This cracking progresses according to the increasing bond energy values. Aliphatic C-C bonds γ to the aromatic rings break first, followed by β bonds, naphtenic and possibly α aliphatic bonds, in all cases following the increasing bond strength. Branches from the opening of naphtenic rings, once formed, crack according to this sequence. The conversion to volatile products measured by weight yield and the coke yield in a thermogram (Fig. 3) and the light product yields (Fig. 4) can be predicted in a reasonable way from the model in this peri-condensed representation of Boscan asphaltenes AMS (Fig.1). However, for the open kata-condensed Athabasca molecular representation (Fig. 2), this trend did not work. The kinetic model invariably went to zero coke due to the complete fragmentation of the Fig. 2 molecule to volatile products. The calculation by quantum mechanical methods of bond energies indicated that the weakest bonds were not the γ or further away aliphatic bonds of aromatic side chains, but instead the C-H bonds in the hydroaromatic substructures to the right side of Fig. 2. When this bond rupture order was allowed, the very first process that occurred was the aromatization of the right side of the molecule in Fig. 2, according to the first six steps in Table 1. This aromatized part was represented by a black circle in Table 1. From this step on, this structure remains as a coke precursor not originally present. The left side totally cracked to produce gases and liquids, as depicted in Table 1 after step 6.

From this kinetic model results, we concluded that this very early aromatization, that introduces a coke precursor nucleus in the molecule, even before liquids and gases are formed, is a very important principle that governs the natural tendency to form coke in complex hydrocarbon systems. It could also explain the increased coke yield of heavy petroleum fractions pretreated by extended periods of time at low temperatures (below 300°C), as reported by Cotte et. al. [20]. Present tendency is toward the consideration of kata-condensed structures, like that of Fig. 2, as more representative of heavy petroleum fractions [18], than those peri-condensed as in Fig. 1. This principle indicates a likely path to coke formation in these open systems, and the expansion of the reaction network in pyrolysis to include it, together with other non-conventional reactions like the retrograde reactions proposed by Mc. Millen and Malhotra [21]. The reasonable agreement between the tendencies in products formation and the conversion and coke yields propose by Sanford for the AMS of Fig. 1 (Fig. 6), indicates the usefulness of the PYRO2 kinetic model and its predictive capability for gross results, in spite of the very simple assumptions it contains. The disagreement with gas and liquid yields, we believe, indicates mainly the failure of the AMS to contain certain reactivity information. This was particularly evident in the CO yield for Boscan asphaltenes. Experimentally, this is one of the first gas product to be formed at about 400 °C, before the bulk of gases peak [17], but the model indicated its formation at about 600 °C, after the bulk gases formation in Fig. 6 (does not appears due to the Y-scale). This disagreement indicates that although the AMS is consistent with the analytical data from which it was builded up, its reactivity is not consistent, and the position of the CO group should be modified accordingly. Improvements in reaction networks and in the AMS's can be made with the use of this model. This should give a deeper knowledge of the chemistry of heavy petroleum fractions, which was the main objective of the development of the PYRO2 model.

4. SUMMARY AND CONCLUSIONS

A kinetic model was developed to study the thermal reactivity of average molecular structures representative of heavy petroleum fractions. This model is based on the application of the Arrhenius equation to the rupture of C-X bonds, arranged by increasing activation energies estimated through quantum mechanical principles and correlations. Reasonable gross agreement was obtained with experimental data and with chemical intuition as applied to the pyrolysis of a crude residue and an asphaltene. This application indicated that:

-The reproduction of the experimental thermogram of the boscan asphaltenes, indicated that the theoretical considerations to obtain the activation energies associated with each step of kinetic model are in reasonable agreement with experimental data.

-The PYRO2 model did not reproduce the distribution of volatile products relieved from the thermogravimetric pyrolytic experiments of the fraction considered. This mismatch of some kinetic model results with experimental data indicated that further improvements or corrections are necessary in the average molecular structures representative of heavy petroleum fractions.

-Early aromatization of certain hydroaromatic moieties, during the thermal treatment of very complex kata-condensed hydrocarbon systems, appears to be an important factor in the natural tendency of heavy crude oil fractions to produce coke. This aromatization should be included as an important further reaction in the networks representative of hydrocarbon systems under pyrolysis conditions.

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Table 1. Pyrolysis scheme derived from the PYRO2 kinetic model for a cracked Athabasca residue Average Molecular Structure.

Step	Molecule	Ea Kcal/Mol	Step	Molecule	Ea Kcal/Mol	Step	Molecule	Ea Kcal/Mol
0		-	12	+ C2	19	24	+ 2Cl	22
1		30	13	+ C2	19	25		22
2		38	14		19	26	+ 2Cl	23
3		33	15		19	27	+	23
4		30	16		20	28	+ +	24
5		30	17		22	29	+	24
6		29	18		22	30	+ 2	24
7		19	19	+ Cl	22	31	+ 2	26
8		19	20	+ C2	22	32	+ Cl +	27
9	+ Cl	19	21		22	33	Coke	-
10		19	22	+ C2	22			
11		19	23		22			

Table 2. Fitting parameters, correlation factor r^2, and standard deviation s for the correlations: BS(A-B) = a + b DE(A-B)

Bond (A-B)	a (Kcal)	b (Kcal/Hartree)	r^2	s (Kcal)
C-C	-95.371	1339.273	0.95	16.8
C-S	-31.952	998.201	0.94	5.7
C-H	-414.488	4837.562	0.94	5.7

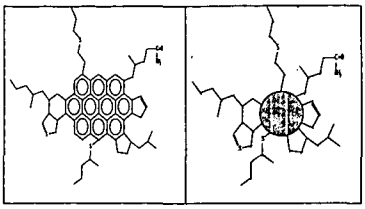

Fig.1. The Boscan Asphaltene Average Molecular Structure (from Ref. 17) and its Compact Representation

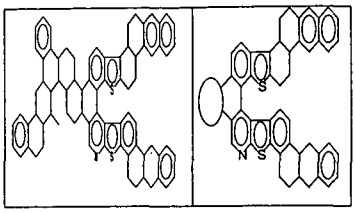

Fig.2. The Average Molecular Structure of an Athabasca Cracked Residue (from Ref.18) and its Compact Representation.

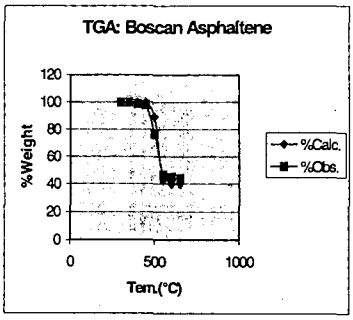

Fig.3. Calculated (from PYRO2 model) and Observed (form Ref. 17) TGA of Boscan Asphaltene.

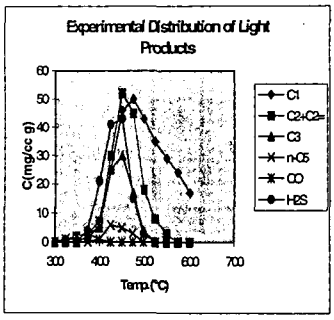

Fig.4. Experimental Distribution of Light Products from the pyrolysis of Boscan Asphaltenes. Data from Ref. 17

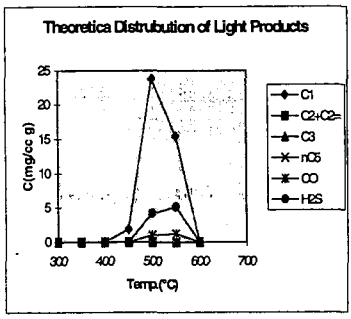

Fig.5. Theoretical Distribution of Light Products from the pyrolysis of Boscan Asphaltenes obtained from PYRO2 Model.

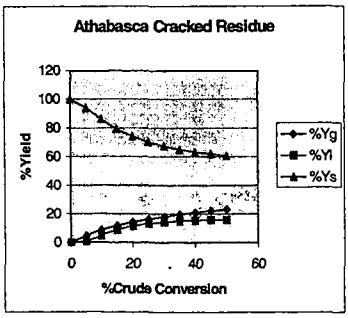

Fig.6. Gas (Yg), liquid (Yl) and residue plus solids (Ys) yields calculated from the PYRO2 kinetic model for the Athabasca Residue.