MODELING PYROLYSIS AND CARBONIZATION OF PETROLEUM DISTILLATION RESIDUES IN DELAYED COKING OPERATIONS

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Abstract

For understanding the interaction between process conditions and the mechanical behavior of semi batch reactors dedicated to the pyrolysis and carbonization of petroleum distillation residues, it is necessary to select a simple method of characterization of residues, an effective kinetic model of pyrolysis and suitable methods for estimating accurately thermochemical properties of substances and free radicals involved in the process. In this work, we compare Group Contribution Methods (Joback and Benson) and Molecular Simulation Methods (implemented in the Mopac and the Titan software) for estimation of properties. An empirical kinetic scheme is compared with a micro-kinetic model based on the free radical mechanism of pyrolysis. The preliminary comparison with published pilot plant data indicates that reactor modeling at low conversions can be done with Arrhenius parameters estimated using Benson's group contribution method. Some pyrolysis processes for the upgrade of distillation residues are performed in two sequential units in order to optimize the delicate balance between selectivity and campaign time caused by the parallelism between radical decomposition and condensation reactions (e.g. delayed coking). Since differences in product quality at high conversions are known to be feed and conversion dependent, another implication of the results presented here is that, in the case of these processes, the changes responsible for the differences take place mainly in the downstream unit, in spite of the fact that substantial conversion can occur in the upstream unit.

Introduction

The profitability of petroleum refining plants is strongly influenced by their capability to convert heavy fractions, with low added value, into light fractions of a higher added value. Towards this end, the delayed coking processes are widely utilized for converting petroleum distillation residues through pyrolysis and carbonization, especially in the refining of heavy oils. In the delayed coking process, the vacuum distillation residue of petroleum, sometimes diluted with decanted oils, is mixed with a recycle stream of pyrolysis products and is then sent to a fired heater where the pyrolysis reactions start. By carefully designing the tubes for high velocities and by using large surface to volume ratios, the reactions can be controlled for the purpose of restraining the coke deposition in the furnace as much as possible until the reacting mixture reaches the coking drums. The products are then fractionated, lighter products are sent to other parts in the refinery for further treatment and the heavy bottom product is recycled. The process is semi-continuous because condensation reactions cause coke to accumulate

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as a porous bed in the drum. When full, the output from the furnace diverts to a parallel drum, which has already been cleaned, tested and pre-heated. The drum removed from the operation is steam stripped, quenched with water, drained and cleaned.

The fired heater can be considered as a continuous tubular reactor for initial pyrolysis while the coking drums act as semi batch reactors conducting pyrolysis and carbonization of residues. The mechanical behavior of these reactors is closely dependent on the process conditions. It is important to take into account the interactions between chemistry, mechanical design and process operations to understand how transient conditions during start-up and shut-down influence the mechanical configuration of the equipment.

One of the authors (Sugaya, 1999) has recently modeled the heat transfer in bulk pyrolysis and carbonization reactors and has explored the interaction between process conditions and thermal stresses. Maciel and Sugaya (2001) have simulated the fired heater using an empirical kinetic scheme where the reactants and products are lumped heuristically, based on pilot plant data. In order to design, operate, control and optimize these processes, it is necessary to develop mechanistic and kinetic models that allow understanding, explaining besides representing pyrolysis reactions of distillation residues. Presently we are implementing micro kinetic models that describe the process chemistry in a more useful and detailed manner. It is also necessary to estimate more accurately the relevant thermochemical properties of substances and free radicals involved in the process.

In this work, Group Contribution Methods and Molecular Simulation Methods are compared for the estimation of standard- heat of formation (ΔH_f^o) for substances and free radicals. Based on a systematic comparison, the group contribution method of Benson (1976) was chosen. The accuracy of the estimate is improved by correlating calculated value with experimental data. Further the kinetic constants of a microkinetic scheme based on a free radical mechanism are compared with the lumped constants obtained from pilot plant data. This work is a part of the ongoing efforts to develop a methodology for simulating simultaneously the coking process and the thermal stresses of the vessels.

Estimation of Thermochemical properties

We calculated the standard heats of formation at 298 K of several pure substances, sixty-three aliphatic hydrocarbons and fourteen aromatics by the following methods,

1. The group contribution method of Joback and Reid (1987)
2. The group contribution method of Benson (1976)
3. The molecular simulation method, PM3 using the commercial software TITAN (1999).

The calculated values (**Hc**) were then compared with experimental values (**He**) reported in Perry (1994). To improve the accuracy of estimation, the experimental values were linearly regressed with the calculated values for each class of substances. The coefficients and the standard deviation of the regression (R^2) are shown in the figures. The estimates of Benson's method and of TITAN simulation show excellent linear correlation with experimental values for aliphatic hydrocarbons (Figure 1). For aromatics (Figure 2) the agreement is good, with R^2 >0.99. The improvement in correlation is mainly due to grouping of similar compounds into families.
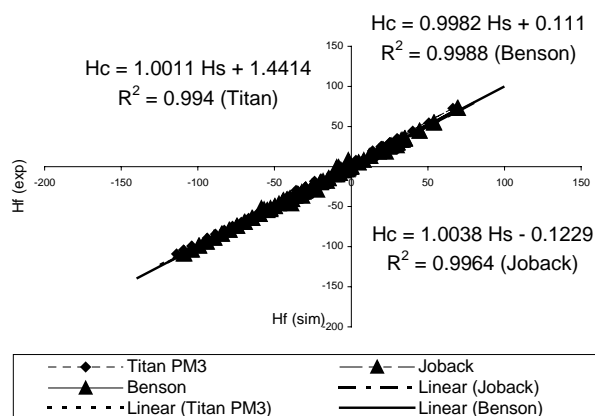

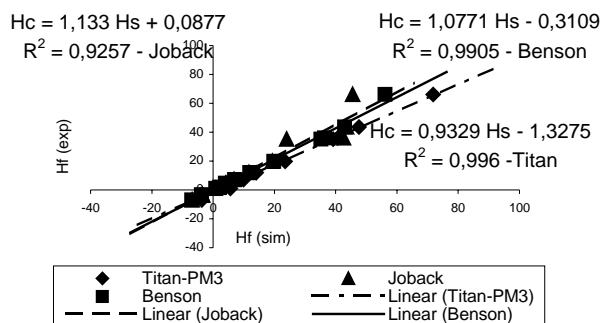*Figure 1 Heat of Formation for Aliphatic Hydrocarbons at 298 K (kcal/mol)*

Figure 2 Heat of Formation for Aromatics at 298 K (kcal/mol)

Standard heats of formation of several families of radicals calculated with the group contribution method of Benson and the molecular simulation method PM3 were compared with the molecular simulation calculations made by Ma and Schoebert (2000), using MOPAC software and with the experimental values. The results for primary radicals are shown in figure 3. Figure 4 shows the results for secondary and tertiary radicals. Figure 5 shows the results for cyclo-alkyl radicals

Again the estimates were regressed linearly with the experimental standard-state heats of formation of free

radicals. Since the experimental measurement of the heat of formation for free radicals is difficult to perform due to their instability, high reactivity and short life-time, correlations have been developed from the available literature data to estimate, with some accuracy, heats of formation for free radicals which are not available. The correlations derived from Benson's method exhibited equal or more accurate results when compared with those using estimates from commercial software (TITAN, MOPAC). Moreover these commercial programs need a special interface for exchanging information with other simulation routines (developed in Fortran 90, for example).
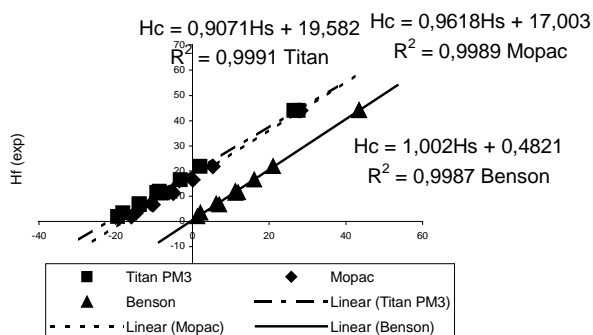

Hc = 0,9071Hs + 19,582
R^2 = 0,9991 Titan
Hc = 0,9618Hs + 17,003
R^2 = 0,9989 Mopac
Hc = 1,002Hs + 0,4821
R^2 = 0,9987 Benson

Figure 3 Heat of Formation for Primary Aromatic Radicals at 298 K (kcal/mol)

Hc = 0,9727Hs + 14,036
R^2 = 0,9924 Titan
Hc = 0,9507Hs + 12,093
R^2 = 0,994 Mopac
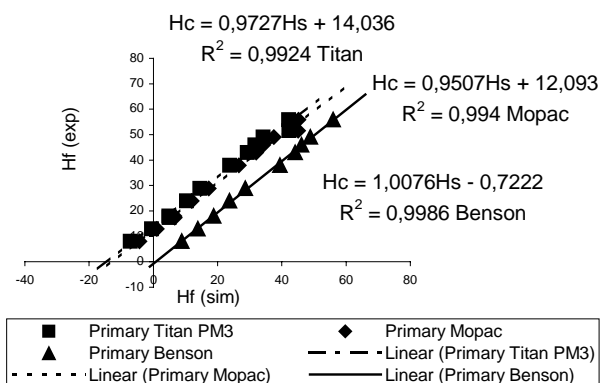Hc = 1,0076Hs - 0,7222
R^2 = 0,9986 Benson

Figure 4 Heat of Formation for Secondary and Tertiary Radicals at 298 K (kcal/mol)

Reactor Model and Kinetic Scheme

We consider the reported data for pyrolysis of two vacuum residues in pilot plant experiments. Table 1 shows the principal characteristics of residues studied in the pilot plant. The kinetics was modeled empirically by first order rates using lumped components of the product from the fired heater. Figure 6 shows the kinetic constants for pyrolysis of resid 2 estimated from a set of pilot plant data of product yields with time at different temperatures (Sugaya, 1999).

For the simulation of fired heater, we have adopted a dual plug flow reactor description (DPFR) of Maciel and Sugaya (2001) in which the residence times of coexisting phases are taken into account by two parallel plug flows of vapor and liquid traveling axially at different rates. The residues were characterized according to the methodology developed by Dente et al. (1997), Bozzano et al. (1998) and McGreavy and Sugaya (1998).

The kinetic scheme and the kinetic constants for the vapor phase proposed by Ranzi et al (2001) were adopted .
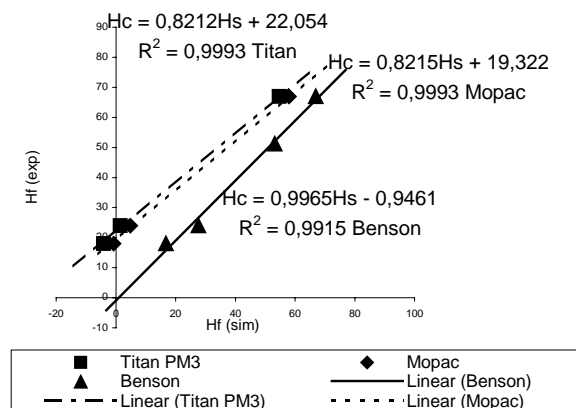

Hc = 0,8212Hs + 22,054
R^2 = 0,9993 Titan
Hc = 0,8215Hs + 19,322
R^2 = 0,9993 Mopac
Hc = 0,9965Hs - 0,9461
R^2 = 0,9915 Benson

Figure 5 Heat of Formation for Cycloalkyl Radicals at 298 K (kcal/mo)l

. The reaction scheme can be summarized as:
I) Radical formation: AB → A• + B•
II) Propagation II A) Radical Decomposition : A-CH•-CH2-B → A-CH=CH2 + B• II B)Hydrogen Abstraction A• +HB → AH+ B•
 III) Termination: A• + B•:→ AB

Where AB is a model compound representing the petroleum fraction.

Table 1. Characteristics of feeds for pyrolysis

Feed	Res. 1	Res 2
Density (°API)	8.60	3.73
Watson Characterization Factor*	11.45	11.32
Conradson Carbon Residue (%wt)	18.6	24.3
Molecular Weight (MW)	810	1120
Sulfur (%wt)	4.65	5.53

* units (R)^(1/3) /° API

The kinetic constants were corrected for the liquid phase as follows $k_{liquid} = k_{vapor} \exp\left[(\Delta S^a / R) - (\Delta H^a / RT)\right]$ where ΔSa = -33 J/K-gmol and ΔHa = -1300$\sqrt{MW}$ J/.gmol [Bozzano (1994)]. The products were lumped in the same manner as for pilot plant data. The kinetic constants were computed for different steps Assuming Arrhenius relation

the effective activation energies were calculated from Figure 6 for pilot plant experiments. In this preliminary work, one of the propagation steps was considered to be dominant and yields were simulated. Again the kinetic constants and activation energies were calculated based on the liquid product yields.

Table 2 compares the activation energies obtained from pilot plant data and the values obtained by considering dominant steps of the micro kinetic scheme. All the values are in kcal per mole of feed. The activation energy estimated from experiments approximates the estimates made from a microkinetic scheme where the initial pyrolysis is dominated by alkyl radical decomposition to form methyl radical or a primary radical. As the pre factors of the kinetic constants are of same magnitude for different reaction steps, we can conclude that decomposition reactions to form primary radicals control the reaction kinetics in the fired heater
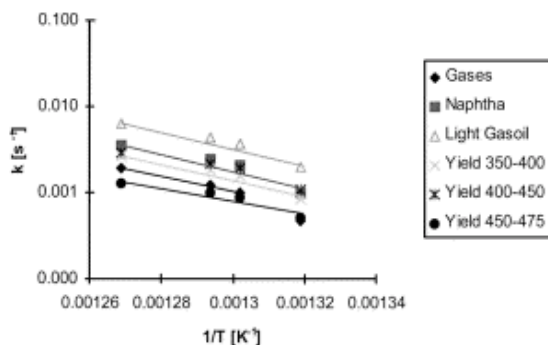

Figure 6. Kinetic constants for Resid 2 from experimental data

Table 2. Activation energies (kcal/mole of feed)

Component	Resid 1	Resid 2
Gases	41919	42343
Naphtha	43742	46578
Light gasoil	43742	46578
yield 350-400	43742	42343
yield 400-450	40097	40226
yield 450-475	38274	40226
Feed	41919	43049
Microkinetics	42415*	43983*
	40915**	42483**

*Assuming the initial pyrolysis is dominated by alkyl radical decomposition to form methyl radical. ** Assuming the initial pyrolysis is dominated by alkyl radical decomposition to form primary radical

Conclusions

For proper understanding of delayed coking process, it is necessary to use an adequate method of characterization of residues and an effective kinetic model of pyrolysis, and also to estimate precisely the thermo-chemical properties of substances and free radicals involved in the process. We have found that the standard heat of formation for

substances and free radicals of pyrolysis can be estimated by first calculating a trial value by Benson's method (1976) and then substituting this value in the linear relation proposed for the corresponding class to empirically improve the accuracy of estimate.

The pilot plant data is consistent with the microkinetic scheme proposed by Ranzi et al (2001) for mild pyrolysis of petroleum distillation residues under isothermal conditions. With this scheme it is possible to identify the controlling reaction steps. The present kinetic scheme can be readily extended for different feeds unlike the earlier empirical scheme of Maciel and Sugaya (2001).

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