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THE CHEMISTRY AND PHYSICS OF COKING

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Abstract – The causes of coke formation during petroleum refining are only now beginning to be understood. They are closely related to the mechanism of the thermal decomposition of the petroleum constituents and to changes in the character of the liquid medium. It was formerly believed that coke formation was a polymerization reaction whereupon the chemical precursors to coke immediately formed macromolecules when subject to the processing temperatures. This is not so. And it is the initial stages of the thermal decomposition which determine the ultimate path of the reaction. Coke formation is a complex process involving both chemical reactions and thermodynamic behavior. Reactions that contribute to this process are cracking of side chains from aromatic groups, dehydrogenation of naphthenes to form aromatics, condensation of aliphatic structures to form aromatics, condensation of aromatics to form higher fused-ring aromatics, and dimerization or oligomerization reactions. Loss of side chains always accompanies thermal cracking, and dehydrogenation and condensation reactions are favored by hydrogen deficient conditions.

Key words: *Petroleum, Coking, Cracking, Phase Separation*

INTRODUCTION

Crude oil is rarely used in its raw form but must instead be converted into its various products, some with a hydrogen content different from that of the original feedstock (Fig. 1). This is achieved by application of a variety of refining processes. Thus, the chemistry of the refining process is concerned primarily with the production not only of better products but also of salable materials.

A refinery is a complex network of integrated unit processes for the purpose of producing a variety of products from crude oil (Fig. 2). Refined products establish the order in which the individual refining units will be introduced, and the choice from among several types of units and the

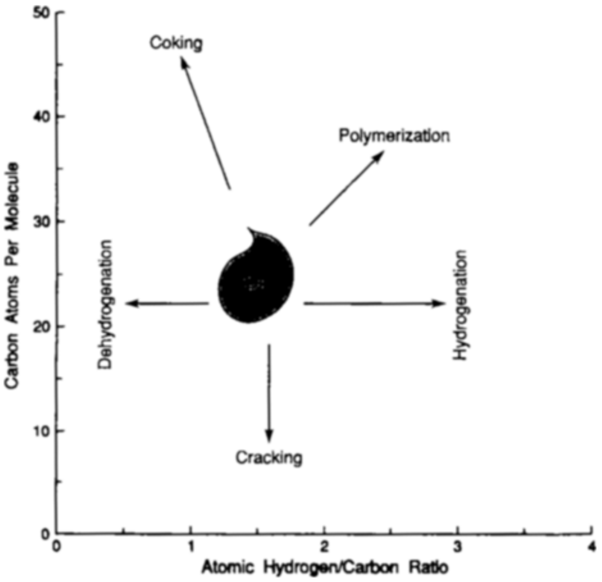

Fig. 1. Variation in hydrogen content of crude oil and crude oil products.

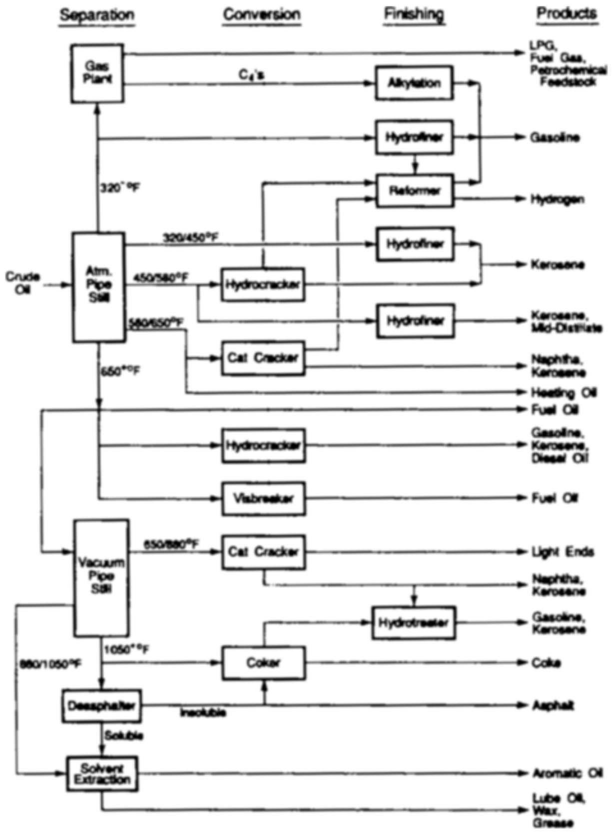

Fig. 2. Schematic representation of a petroleum refinery showing the relative placement of the various processes.

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size of these units is dependent upon economic factors. The trade-off among product types, quantity, and quality influences the choice of one kind of processing option over another.

Thermal cracking processes are commonly used to convert petroleum residua into volatile liquid products. Examples of modern thermal cracking processes are *visbreaking* and *coking* (*delayed coking, fluid coking*, and *flexicoking*) [Speight, 1991; Gray, 1994]. These processes effect various levels of conversion of the feedstock (Fig. 3) under a variety of conditions (Fig. 4). In all of these processes the simultaneous formation of sediment or coke limits the conversion to usable liquid products [Speight, 1992].

The causes of coke formation are only now beginning to be understood. They are closely related to the mechanism of the thermal decomposition of the petroleum constituents and to the change in the character of the liquid medium. Any chemical or physical interaction that causes a change in the solubility parameter of the solute relative to that of the solvent will also cause *incompatibility* be it called *instability, phase separation, sediment formation*, or *sludge formation.*

Instability or *incompatibility*, resulting in the separation of solids during refining, can occur during a variety of processes, either by intent (such as in the deasphalting process) or inadvertently when the separation is detrimental to the process [Mushrush and Speight, 1995]. Thus, separation of solids occurs whenever the solvent characteristics of the liquid phase are no longer adequate to maintain polar and/or high molecular weight material in solution. The current focus is on the formation of coke (or sediment) in a reactor, which occurs when the solvent characteristics of the liquid medium change so that insoluble material appears as a separate phase.

The formation of solid sediment, or coke, during thermal processes is a major limitation on processing. Furthermore, the presence of different types of solids shows that solubility controls the formation of solids. And the tendency for solid formation changes in response to the relative amounts of the light ends, middle distillates, and residues and to their changing chemical composition during the process [Gray, 1994]. In fact, the prime mover in the formation of incompatible products during the processing of feedstocks containing asphaltenes is the nature of the primary thermal decomposition products, particularly those designated as *carbenes* and *carboids* [Speight, 1987, 1992; Wiehe, 1992, 1993a, b].

Thus, the challenges facing process chemistry and physics are determining (1) the means by which petroleum constituents thermally decompose, (2) the nature of the products of thermal decomposition, (3) the subsequent decomposition of the *primary* thermal products, (4) the interaction of the products with each other, (5) the interaction of the products with the original constituents, and (6) the influence of the products on the composition of the liquids.

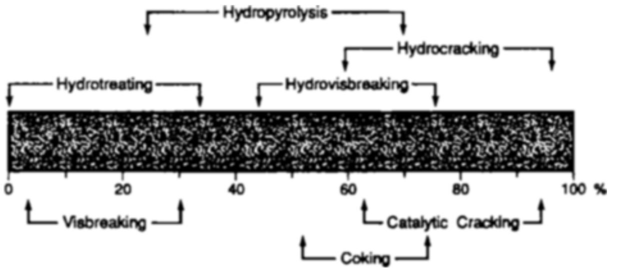

Fig. 4. Temperature and pressure ranges for various refinery processes.

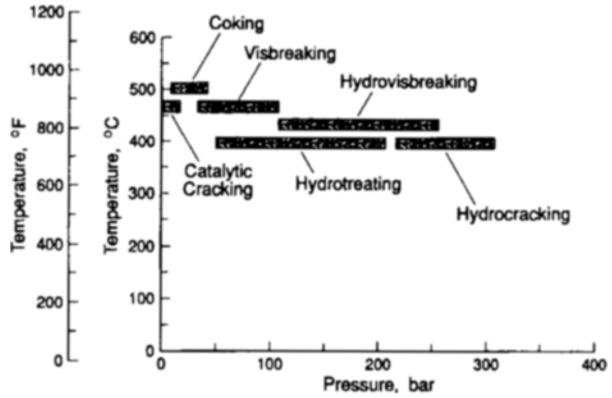

Fig. 3. Levels of conversion of various refinery processes to liquid products.

PROCESS CHEMISTRY

For convenience, and in order to understand processing behavior, crude oil is often sub-divided into a variety of fractions (Fig. 5). These fractions are named according to the method of separation and the name does not often accurately reflect the chemical nature of the fraction [Long and Speight, 1997]. Nevertheless, each fraction of a heavy feedstock is capable of producing coke when it is subject to a thermal process (Fig. 6).

There are various theories relating to the thermal decomposition of organic molecules and this area of petroleum technology has been the subject of study for several decades [Hurd, 1929; Fabuss et al., 1964; Fitzer et al., 1971]. The relative reactivity of petroleum constituents can be assessed on the basis of bond energies but the thermal stability of an organic molecule is dependent upon the bond strength of the weakest bond. And even though the use of bond energy data is a method for predicting the reactivity or the stability of spe-

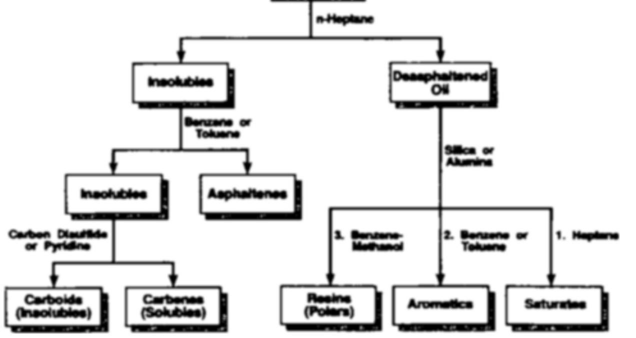

Fig. 5. A general fraction scheme for refinery feedstocks.

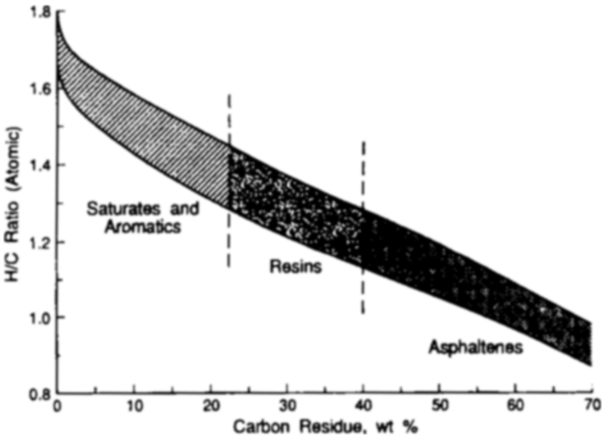

Fig. 6. Relationship of thermal coke yields to the hydrogen-to-carbon (H/C) atomic ratio.

cific bonds under designed conditions, the reactivity of a particular bond is also subject to its environment. Thus, it is not only the reactivity of the constituents of petroleum that is important in processing behavior, it is also the stereochemistry of the constituents as they relate to one another that is also of some importance. It must be appreciated that the stereochemistry of organic compounds is often a major factor in determining reactivity and properties [Eliel and Wilen, 1994].

The chemistry of conversion process may be quite complex [King et al., 1973; Speight, 1984], and an understanding of the chemistry involved in the conversion of a crude oil to a variety of products is essential to an understanding of refinery operations. The complexity of the individual reactions occurring in an extremely complex mixture and the *interference* of the products with those from other components of the mixture is unpredictable. Or the *interference* of secondary and tertiary products with the course of a reaction and, hence, with the formation of primary products may also be cause for concern. Hence, caution is advised when applying the data from model compound studies to the behavior of petroleum, especially the molecularly complex heavy oils. These have few, if any, parallels in organic chemistry. Coke formation is considered, with just cause to be the result of malignant side reactions of thermal processing. Of these reactions, most will produce carbene/carboid-type species that can produce other products. In processes involving catalysts, the most damaging product is one which remains on the catalyst surface and cannot be desorbed and results in the formation of coke, or remains in a non-coke form but effectively blocks the active sites of the catalyst.

In a mixture as complex as petroleum, the reaction processes can only be generalized (Fig. 7) because of difficulties in analyzing not only the products but also the feedstock as well as the intricate and complex nature of the molecules that make up the feedstock. The formation of coke is detrimental to process efficiency and to catalyst performance [Speight, 1987; Dolbear, 1997].

Refining the heavier feedstocks has become a major issue in modem refinery practice. The limitations of processing heavy oils and residua depend to a large extent on the amount of higher molecular weight constituents (i.e., asphaltenes) present in the feedstock that are responsible for high yields of thermal and catalytic coke [Speight, 1981, 1984; Teman, 1983; LePage and Davidson, 1986]. Each fraction of petroleum has the potential to produce thermal coke in yields varying from almost zero to more than 60 % w/w (Fig. 8).

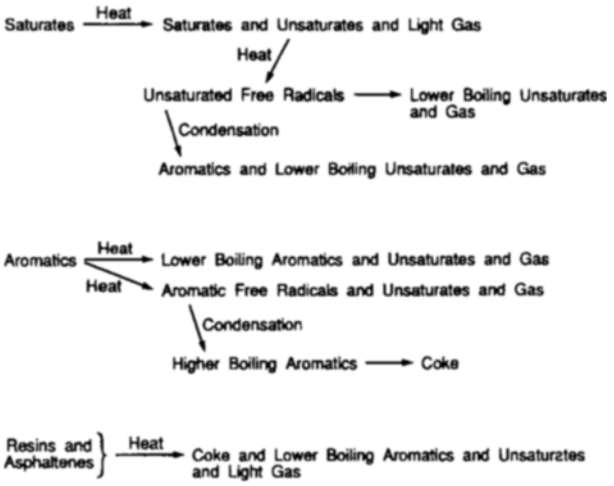

Fig. 7. General chemistry of the thermal decomposition of crude oil fractions.

When petroleum is heated to temperatures in excess of 350 °C (660 °F), the rate of thermal decomposition of the constituents increases significantly. The higher the temperature, the shorter the time to achieve a given conversion and the *severity* of the process conditions is a combination of residence time of the crude oil constituents in the reactor and the temperature needed to achieve a given conversion. Because of the tendency to form high yields of thermal coke, there has been considerable focus on the thermal chemistry of the asphaltene constituents [Magaril and Aksenova, 1968, 1970; Magaril and Ramazaeva, 1969; Magaril et al., 1970, 1971; Schucker and Keweshan, 1980; Shiroto et al., 1983; Speight, 1997 and references cited therein].

Briefly, the asphaltene constituents undergo thermal reaction to produce nonvolatile coke [Speight, 1970, 1989; Vercier, 1981]. In a very general scheme, the chemistry of asphaltene coking has been suggested to involve the thermoly-

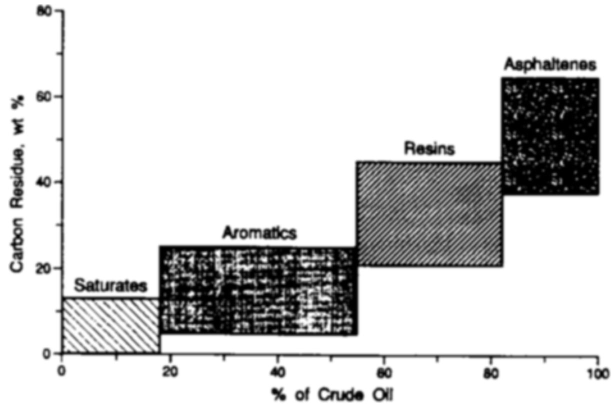

Fig. 8. Range of thermal coke yields for individual heavy crude oil fractions and sub-fractions.

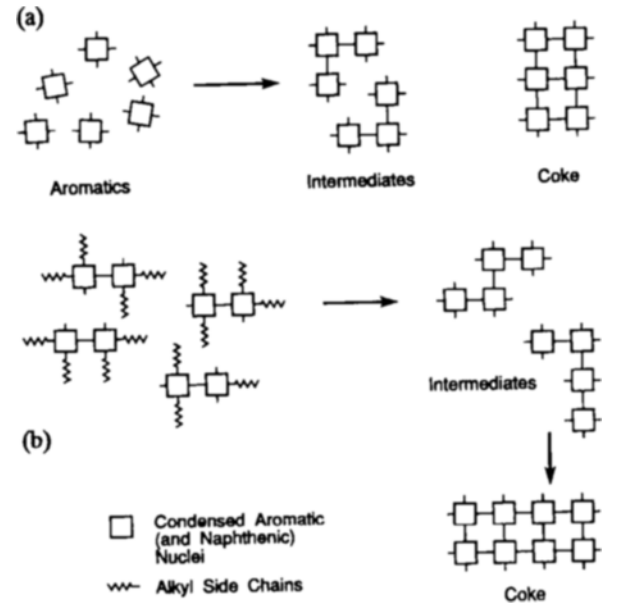

Fig. 9. Schematic representation of coke formation: (a) the condensation mechanism and (b) the mechanism involving de-alkylation and the formation of lower molecular weight polar species prior to the formation of coke.

sis of thermally labile bonds to form reactive species that react with each other (condensation) to form coke (Fig. 9).

The initial reactions in the coking of petroleum feedstocks that contain asphaltenes involve the thermolysis of asphaltene aromatic-alkyl systems to produce volatile species (paraffins and olefins) and nonvolatile species (aromatics) leading to a relationship between asphaltenes content and carbon residue formation [Speight, 1987; Roberts, 1989; Schabron and Speight, 1997b]. In addition, the formation of liquid hydrocarbon products creates region of instability causing the highly aromatic and highly polar (refractory) products separate from the surrounding oil medium as an insoluble phase and proceed to form coke (Fig. 10).

Thermal studies using model compounds confirm that volatility of the fragments is a major influence in carbon residue formation and a pendant-core model for the high molecular weight constituents of petroleum has been proposed [Wiehe, 1994]. In such a model, the scission of alkyl side chains occurs thereby leaving a polar core of reduced volatility and leads to the formation of a carbon residue [Speight, 1992, 1994; Wiehe, 1994]. In addition, even one-ring aromatic cores can produce a carbon residue if multiple bonds need to be broken before a core can volatilize [Wiehe, 1994].

Nitrogen species also appear to contribute to the pattern of the thermolysis. For example, the hydrogen or carbon-carbon bonds to adjacent to a ring nitrogen undergo thermolysis quite readily, as if promoted by the presence of the nitrogen atom [Fitzer et al., 1971; Speight, 1997]. If it can be assumed that heterocyclic nitrogen plays a similar role in the thermolysis of asphaltenes, the initial reactions therefore involve thermolysis of aromatic-alkyl bonds that are enhanced by the presence of heterocyclic nitrogen. An ensuing series of secondary reactions, such as aromatization of naphthenic species and condensation of the aromatic ring systems, then leads to the production of coke. Thus, the initial step in the formation of coke from asphaltenes is the formation of volatile hydrocarbon fragments and nonvolatile heteroatom-containing systems.

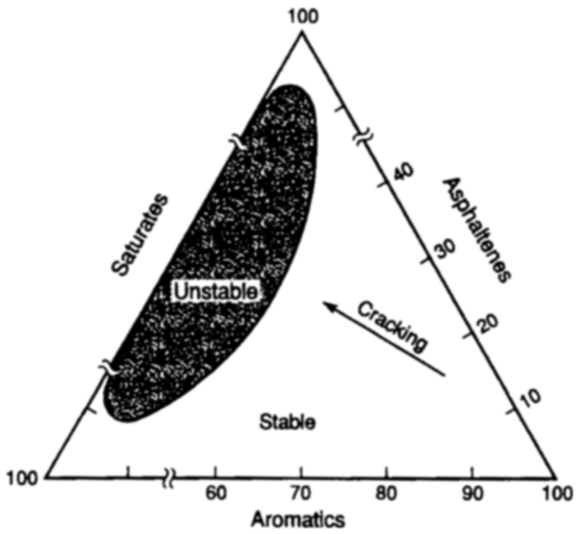

Fig. 10. Representation of the formation of an unstable region during thermal decomposition of crude oil due to de-alkylation of the high molecular weight species.

It has been reported that as the temperature of an asphaltene solution is raised from 100°C (212°F) to 400°C (750 °F) there is a progressive decrease in the size of the asphaltenes particle [Thiyagarajan et al., 1995]. Furthermore, there is also the inference that the structural integrity of the asphaltene particle is compromised and that irreversible thermochemistry has occurred. Indeed, that is precisely what is predicted and expected from the thermal chemistry of asphaltenes and molecular weight studies of asphaltenes [Rao and Serrano, 1986; Speight, 1991].

It is also interesting to note that although the aromaticity of the asphaltenes is approximately equivalent to the yield of

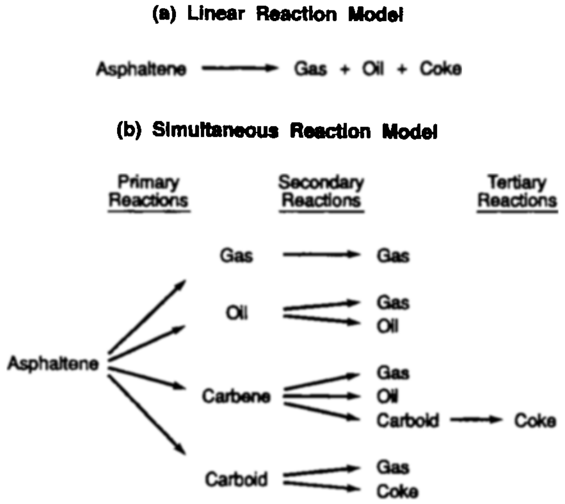

Fig. 11. Representation of the thermal decomposition of asphaltenes showing the older linea model and the more acceptable multi-reaction model.

thermal coke (Fig. 6), not all the original aromatic carbon in the asphaltenes forms coke. Volatile aromatic species are eliminated during thermal decomposition, and it must be assumed that some of the original aliphatic carbon plays a role in coke formation. The process can be represented as involving a multi-reaction sequence (Fig. 11) [Speight, 1987]. Little has been acknowledged here of the role of low-molecular-weight polar species (resins) in coke formation. However, it is worthy of note that the resins are presumed to be lower molecular weight analogs of the asphaltenes. This being the case, similar reaction pathways may apply.

MECHANISM OF COKE FORMATION

Coke formation during the thermal treatment of petroleum residua is postulated to occur by a mechanism that involves the liquid-liquid phase separation of reacted asphaltenes (which may be *carbenes*) to form a phase that is lean in abstractable hydrogen. The unreacted asphaltenes were found to be the fraction with the highest rate of thermal reaction but with the least extent of reaction. This not only described the appearance and disappearance of asphaltenes but also quantitatively described the variation in molecular weight and hydrogen content of the asphaltenes with reaction time. Further evidence for the liquid-liquid phase separation was the observation of spherical particles of liquid crystals.

One of the postulates of coke formation involves the production of coke by a sequence of polymerization and condensation steps from the lightest (lower molecular weight) to the heaviest (higher molecular weight) fractions. Present evidence [Speight, 1992, 1994; Wiehe, 1992, 1993a, b] shows that the reaction pathway of the asphaltenes to coke is much more complex and involves at least several reaction stages [Speight, 1997].

Several kinetic studies have concentrated on the conversion of the asphaltene portion of petroleum residua. One in particular [Schucker and Keweshan, 1980] showed that asphaltenes exhibit a coke induction period when thermally converted at 400 °C (750 °F), but the kinetic model did not include a coke-formation step. Other workers [Savage et al., 1985, 1988] also observed a coke-induction period for the thermolysis of asphaltenes that disappeared when the thermolysis temperature was raised to 450 °C (840 °F). It was proposed [Savage and Klein, 1989] that toluene-insoluble coke could be defined as a molecular species with a molecular weight of greater than 300 and an hydrogen-to-carbon atomic ratio less than 1.

More recently [Wiehe, 1993a, b], a kinetic model was developed that describes four common features of residua thermal conversion kinetics. These features are:

1. an induction period prior to coke formation,
2. a maximum concentration of asphaltenes in the reacting liquid,
3. a decrease in the asphaltene concentration that parallels the decrease in heptane-soluble material, and
4. the high reactivity of the unconverted asphaltenes.

In addition, there is an induction period during which no coke is formed and many kinetic models that contain sequences of direct chemical reactions to coke fail to predict the induction period. This induction period has been observed experimentally by many previous investigators [Levinter et al., 1966, 1967; Magaril and Aksenova, 1968; Magaril and Aksenova, 1970; Valyavin et al., 1979; Takatsuka et al., 1989a] and makes visbreaking possible. The postulation that coke formation is triggered by the phase separation of asphaltenes [Magaril et al., 1971] led to the use of linear variations of the concentration of each fraction with reaction time, resulting in the assumption of zero-order kinetics rather than first order kinetics.

This model represents the conversion of asphaltenes over the entire temperature range and of heptane-soluble materials in the coke induction period as first-order reactions. The data also show that the four reactions give simultaneously lower aromatic and higher aromatic products, on the basis of other evidence [Wiehe, 1992]. Also, the previous work showed that residua fractions can be converted without completely changing solubility classes [Magaril et al., 1971] and that coke formation is triggered by the phase separation of converted asphaltenes.

The maximum solubility of these product asphaltenes is proportional to the total heptane-soluble materials, as suggested by the observation that the decrease in asphaltenes parallels the decrease of heptane-soluble materials. Finally, the conversion of the insoluble product asphaltenes into toluene-insoluble coke is pictured as producing a heptane-soluble byproduct, which provides a mechanism for the heptane-soluble conversion to deviate from first-order behavior once coke begins to form. An infinite reaction rate for this coke-forming reaction is used to show that the reaction rate is phase equilibrium controlled:

$$H^+ = aA^* + (1-a)V \qquad \text{reaction constant } k_H$$

$$A+ = mA^* + nH^* + (1-m-n)V \qquad \text{reaction constant } k_A$$

$$\text{solubility limit: } A^*_{max} = SL(H^+ + H^*)$$

$$A^*_{ex} = A^* - A^*_{max}$$

$$A^*_{ex} = (1-y)TI + yH^*$$

where a is a stoichiometric coefficient; A^+, reactant asphaltenes; A^*, asphaltene cores; A^*_{max}, maximum asphaltene cores that can be held in solution; A^*_{ex}, excess asphaltene cores beyond what can be held in solution; H^+, reactant, nonvolatile heptane-soluble materials; H^*, product, nonvolatile heptane-soluble materials; k_A first-order reaction rate constant for reactant asphaltene thermolysis (min^{-1}); k_H, first-order reaction rate constant for the thermolysis of reactant heptane-soluble materials (min^{-1}); m, stoichiometric coefficient; n, stoichiometric coefficient; S_L, solubility limit (wt%/wt%); TI, toluene-insoluble coke; and V, volatile materials.

The first two parallel first-order reactions for the thermolysis of unreacted heptane-soluble materials and unreacted asphaltenes are the only reactions that occur during the coke induction period. During the coke induction period the reactant asphaltenes form only lower molecular weight products and, as long as the asphaltenes remain dissolved, the heptane-soluble materials can provide sufficient abstractable hydrogen to terminate asphaltene free radicals, making asphaltene radical-asphaltene radical recombination infrequent.

In support of this assumption, it is known [Langer et al., 1961] that partially hydrogenated refinery process streams provide abstractable hydrogen and as a result, inhibit coke formation during residuum thermal conversion. Thus, the heptane-soluble fraction of a residuum that contains naturally occurring, partially hydrogenated aromatics, can provide abstractable hydrogen during thermal reactions.

As the conversion proceeds, the concentration of asphaltene cores continues to increase and the heptane-soluble fraction continues to decrease until the solubility limit, S_L is reached. Beyond the solubility limit, the excess asphaltene cores, A^*_{ex}, phase separate to form a second liquid phase that is lean in abstractable hydrogen. In this new phase asphaltene radical-asphaltene radical recombination is quite frequent, causing a rapid reaction to form solid coke and a by-product of a heptane-soluble core.

The asphaltene concentration varies little in the coke induction period but then decreases once coke begins to form. Observing this, it might be concluded that asphaltenes are unreactive, but it is the high reactivity of the asphaltenes down to the asphaltene core that offsets the generation of asphaltene cores from the heptane-soluble materials to keep the overall asphaltene concentration nearly constant.

Previously, it was demonstrated [Schucker and Keweshan, 1980; Savage et al., 1988] that the hydrogen-to-carbon atomic ratio of the asphaltenes decreases rapidly with reaction time for asphaltene thermolysis and then approaches an asymptotic limit at long reaction times, which provides qualitative evidence for asphaltene cracking down to a core.

The measurement of the molecular weight of petroleum asphaltenes is known to give different values depending on the technique, the solvent and the temperature [Dickie and Yen, 1967; Moschopedis et al., 1976; Speight et al., 1985]. As shown by small-angle x-ray [Kim and Long, 1979] and neutron [Overfield et al., 1989] scattering, this is because *separated* asphaltenes tend to self-associate and form aggregates.

There is a need to investigate fully the degree of association of asphaltenes in thermal systems and to determine whether it has any influence on the coke forming tendencies of the asphaltenes. The *association factor*, α [Wiehe, 1993a, b], is the ratio of the associated molecular size of the asphaltene measured in toluene, the poorest solvent required to dissolve the asphaltene, at a relatively low temperature divided by a measure of an *unassociated* molecular weight [Wiehe, 1992].

$$\alpha = \mathrm{m.\ wt}_{toluene,\ 50^\circ\mathrm{C}} / \mathrm{m.\ wt}_{o\text{-}dichlorobenzene,\ 130^\circ\mathrm{C}}$$

The data for the thermolysis reactions [Wiehe, 1993a, b] indicated that the association factor is nearly constant at approximately two, but when coke formation commences the remaining asphaltenes have less tendency to associate. As more and more toluene-insoluble materials are formed, the association factor continually decreases until the remaining asphaltenes show almost no tendency to associate (α=1). However, there is evidence that even if association occurs at the high temperatures involved in thermal decomposition, association may not make any difference to the chemistry of coke formation [Rao and Serrano, 1986; Schabron and Speight, 1997a].

The importance of solvents in coking has been recognized for many years [e.g. Langer et al., 1961], but their effects have often been ascribed to hydrogen donor reactions rather than phase behavior. The separation of the phases depends on the solvent characteristics of the liquid. Addition of aromatic solvents suppresses phase separation, whereas paraffins enhance separation. Microscopic examination of coke particles often shows evidence for mesophases, spherical domains that exhibit the anisotropic optical characteristics of liquid crystals.

This phenomenon is consistent with the formation of a second liquid phase; the mesophase liquid is denser than the rest of the hydrocarbon, has a higher surface tension, and probably wets metal surfaces better than the rest of the liquid phase. The mesophase characteristic of coke diminishes as the liquid phase becomes more compatible with the aromatic material.

The phase separation phenomenon that is the prelude to coke formation can also be explained by use of the solubility parameter, δ, for petroleum fractions and for the solvents. Although little is known about the solubility parameter of petroleum fractions, there has been a noteworthy attempt to define the solubility parameter ranges for different fossil fuel liquids [Yen, 1984; Speight, 1992, 1994].

As an extension of this concept, there is sufficient fragmented data to draw an approximate correlation between hydrogen-to-carbon (H/C) atomic ratio and the solubility parameter for hydrocarbons and the constituents of petroleum [Speight, 1992, 1994]. Recognition that hydrocarbon liquids can dissolve polynuclear hydrocarbons, a case in which there is usually less than a three-point difference between the lower solubility parameter of the solvent and the higher solubility parameter of the solute. Thus, a parallel, or near-parallel, line can be assumed that allows the solubility parameter of the asphaltenes and resins to be estimated (Fig. 12).

By this means, the solubility parameter of asphaltenes can be estimated to fall in the range 9 to 12, which is in keeping

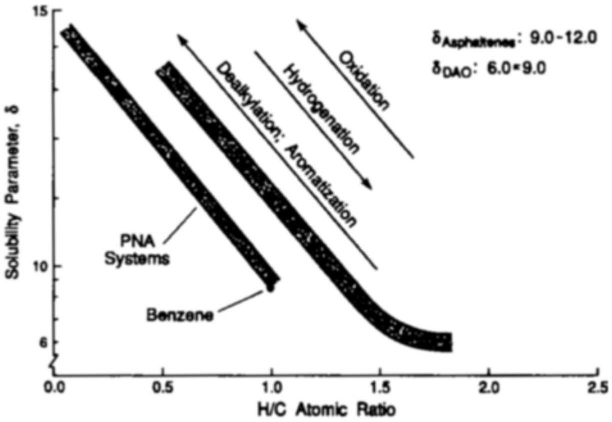

Fig. 12. Relationship of the solubility parameter of petroleum constituents to the hydrogen-to-carbon (H/C) atomic ratio.

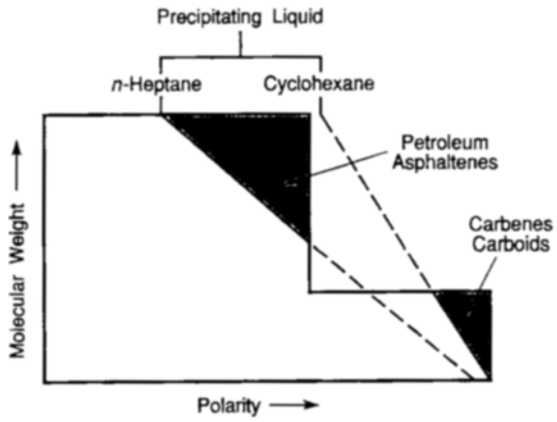

Fig. 13. Representation of asphaltenes as a complex fraction using molecular weight and polarity and the relationship of carbenes (the first thermal decomposition products) to asphaltenes.

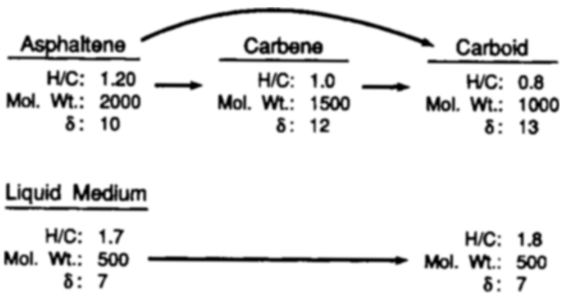

Fig. 14. Representation in the changes solubility parameter of the asphaltenes/carbenes/carboids during thermal decomposition and solubility parameter of the liquid medium.

with the asphaltenes being composed of a mixture of different compound types with an accompanying variation in polarity. Removal of alkyl side chains from the asphaltenes decreases the hydrogen-to-carbon atomic ratio [Speight, 1992; Wiehe, 1993a, b; Gray, 1994] and increases the solubility parameter thereby bringing about a concurrent decrease of the asphaltene product in the hydrocarbon solvent.

In fact, on the molecular weight polarity diagram for asphaltenes, carbenes and carboids can be shown as lower molecular weight, highly polar entities in keeping with molecular fragmentation models (Fig. 13) [Speight, 1992, 1994]. As the thermal decomposition proceeds, the asphaltenes form carbenes and then carboids. This is accompanied by an increase in the solubility parameter of the carbene-carboid products relative to the asphaltenes (Fig. 14). At the same time, the parameter of the liquid medium decreases because of the formation of aliphatic hydrocarbon products. When the differential between the solubility parameter of these thermal products becomes too great [Mitchell and Speight, 1973], and phase separation occurs and coke formation ensues. Obviously, attempts to mitigate coke formation must be taken during the induction period between the onset of thermal decomposition of the asphaltenes and the commencement of phase separation.

When catalytic processes are employed, complex molecules (such as those that may be found in the original asphaltene fraction) or those formed during the process, are not sufficiently mobile (or are too strongly adsorbed by the catalyst) to be saturated by the hydrogenation components. Hence, these molecular species continue to condense and eventually degrade to coke. These deposits deactivate the catalyst sites and eventually interfere with the process.

An additional corollary to this work is that conventional models of petroleum asphaltenes (which, despite evidence to the contrary, invoked the concept of a large polynuclear aromatic system) offer little, if any, explanation of the intimate events involved in the chemistry of coking. Models that invoke the concept of asphaltenes as a complex solubility class with molecular entities composed of smaller polynuclear aromatic systems are more in keeping with the present data [Speight, 1992].

CONCLUSIONS

On the basis of recent work, coke formation during petroleum processing is no longer considered a process on which polymerization of aromatic species occur in the initial stages of the reaction. The initial reactions involve scission of labile bonds to produce aliphatic species and highly polar aromatic products. It is the polar aromatic species that form a separate phase after which coke formation occurs.

The molecular species within the asphaltene fraction, which contain nitrogen and other heteroatoms (and have lower volatility than the pure hydrocarbons), concentrate in the coke and, in addition, are believed to be prime movers in the production of coke [Speight, 1970, 1987]. Such species, containing various polynuclear aromatic systems, can be denuded of the attendant hydrocarbon moieties and are undoubtedly insoluble [Bjorseth, 1983; Dias, 1987, 1988] in the surrounding hydrocarbon medium. The next step is gradual carbonization of such entities to form coke [Magaril and Aksenova, 1968; Magaril and Ramzaeva, 1969; Magaril et al., 1970; Cooper and Ballard, 1962].

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