Role of Chain Reactions and Olefin Formation in Cracking, Hydroconversion, and Coking of Petroleum and Bitumen Fractions

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Received October 8, 2001. Revised Manuscript Received February 4, 2002

Although the mechanism of cracking of distillate fractions is well-known, the reactions that underlay conversion of the residue fractions of petroleum and bitumen are not well defined. Despite the difficulties in analyzing residue fractions in detail, the chemistry of these materials must follow the same elementary reactions as distillates. This paper presents a consistent mechanism for cracking of residues based on the known chemistry of free-radical chain reactions and model compounds. The roles of hydrogen, donor solvents, and added catalysts are then interpreted in this context. The formation of olefin groups from cracking of aliphatic groups gives the potential for addition reactions in the liquid phase. Removal of olefin groups, by reactions with donor solvents or hydrogenation, controls addition reactions and thereby suppresses coke formation. This mechanism suggests that innovative methods to remove or react olefinic groups may allow higher conversion of residues to desirable liquid products.

Introduction

The large reserves of heavy oils and bitumens, in proportion to conventional crude oil, has sparked considerable interest in technologies for converting these feeds into products with more desirable characteristics. In particular, the conversion of the vacuum residue (boiling over 524 °C) into distillates is of particular interest in improving the economic value. Despite the well-established technology for converting these residues by coking or hydroconversion, there is little consensus on the underlying mechanisms of the reaction processes. The objective of this paper is to suggest a mechanism for conversion of these residue materials that is consistent with the fundamentals of chemistry and physics. The tests for consistency are as follows:

1. Each step of the mechanism can be verified from reactions of well-defined chemical components.
2. The mechanism must be consistent with mechanisms for related chemical processes.
3. The mechanism must be consistent with the characteristics of existing process technologies for cracking residue fractions.

Previous proposals of mechanisms for conversion of petroleum residues[1,2] have attempted to explain the observed experimental laboratory results in the context of commercial processes (criterion 3), but they have not applied the other two criteria. The importance of mechanisms in a complex process such as residue conversion is to allow understanding of the performance of existing process technologies and to support innovative design of improved technologies.

Characteristics of Vacuum Residues from Heavy Oils and Bitumens

The residue fraction of these materials is a complex liquid that contains primarily toluene-soluble components, with a low concentration of insoluble minerals and mineral−organic complexes in the case of oilsands bitumen from open-pit mining operations.[3] The solubility of the oil fractions in solvents such as toluene has allowed extensive fractionation and characterization, so that the important chemical substructures are defined.[4−7] Rich in hydrocarbons, the residue fractions contain more than 60% of the carbon in saturated chain and ring structures.[8] The balance of the carbon is in aromatic rings, from one ring up to substituted polycyclic aromatic hydrocarbons. The molecular weights in the residue fraction range from 560 to order 10^3, although considerable controversy continues over the range of molecular weights in these materials.

Clearly, the step at the heart of upgrading processes for residues is cracking the large molecules into smaller, more volatile fragments. The chemistry of the hydrocarbons is very important for this process, but hetero-

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10.1021/ef010243s CCC: $22.00

atoms are also significant. For thermal reactions, the main element of interest is sulfur, which occurs in most residues at concentrations from 1 to 7 wt %.[9] As much as 40% of this sulfur occurs as reactive thioethers and thiolanes in saturated structures.[10] Other elements, including nitrogen, oxygen, vanadium, and nickel, are common in oils but they appear to be less significant to the breakup of large molecules into distillable fragments.

The fraction of vacuum residue that receives the most attention in upgrading is the asphaltenes, defined as the portion of the oil that is insoluble in *n*-pentane or *n*-heptane. This precipitate contains the most polar components in the oil, the largest of the polynuclear aromatic components, and the highest molecular weight species.[11,12] The asphaltene components have a higher concentration of aromatic carbon, sulfur, and other nonhydrocarbon elements than the residue as a whole, but they share a common chemistry. An effective chemical model for asphaltenes and other components in the residue fraction is a random copolymer of aromatic "cores" joined by bridges and attached to pendant groups.[13]

The commercial processes that crack high-boiling components of residues into distillates operate at 410−550 °C where thermal reaction rates are significant. At these conditions, residue feeds are either low-viscosity liquids or vapor−liquid mixtures, depending on the temperature and pressure. Obviously, the higher the temperature the greater the fraction of the feed will enter the vapor phase, but even at the maximum temperatures of commercial processes, a significant portion of the feed will be in the liquid phase. Although vapor-phase reactions can alter yield and product quality in some processes, we can consider reactions in the liquid phase as the primary determinant of the characteristics of residue cracking. In the simplest possible terms, residue conversion concerns the liquid-phase behavior of saturated compounds, alkyl-aromatic , and reactive sulfur groups at thermal reaction conditions.

Related Chemical Processes

One close cousin to residue cracking is the thermal cracking of naphtha to produce olefins. This vapor-phase process is carried out in reaction furnaces at 700−800 °C with very short residence times to maximize the yields of olefins (i.e., alkenes) such as ethylene, propylene, and butenes. The reactions occur by a free-radical chain process, first described by Rice and Hertzfeld[14] and Kosiakoff and Rice[15] for *n*-alkanes. In its simplest form, the reaction cycle is illustrated in Figure 1, where M and $M^{\bullet}$ are the parent alkane and parent radicals, respectively, $R^{\bullet}$ and RH are lower alkyl radicals and the corresponding alkanes, respectively, and A represents olefins. Alkylaromatics and cyclic saturated compounds follow similar reaction pathways.[16,17] Due to their resonance stabilization, aromatic rings do not crack at 410−550 °C, although they participate in hydrogen abstraction and intermolecular rearrangements.

Initiation: $M \xrightarrow{k_1} 2\,R^{\cdot}$ (1)

Propagation:

Hydrogen abstraction $R^{\cdot} + M \xrightarrow{k_2} RH + M^{\cdot}$ (2)

β-Scission $M^{\cdot} \xrightarrow{k_3} R^{\cdot} + A$ (3)

Termination: Radical + Radical → Products (4)

Figure 1. Free-radical chain reaction mechanism for cracking of *n*-alkanes.

Due to the number of possible atoms that can participate in these reactions, even simple compounds give rise to many possible reaction steps and numerous radical intermediates. Despite the complexity of the mixed reactants, the free-radical chain reactions have been modeled in molecular detail using the basic reaction cycle in eqs (1)−(4) of Figure 1, with the addition of isomerization reactions.[18]

Extending the same chemistry into liquid-phase reactions of high molecular weight species, several investigators have considered the thermal cracking of polymers. The detailed kinetics of these liquid-phase reactions have been analyzed as free-radical chain reactions that follow the general Rice-Hertzfeld formalism of Figure 1, with addition of intermolecular reactions, reversible polymerization−depolymerization steps,[19] and coupling between chain reactions in cracking of mixtures of polyethylene and polystyrene.[20]

A third chemical process that has had a tremendous influence on the theories regarding cracking of petroleum residues is the liquefaction of coal. In the solvent-based processes, a hydrogenated solvent is mixed with coal, and possibly a catalyst, at temperatures of 440−490 °C. Coal has a much higher initial molecular weight than residue, therefore, it is present in the reaction mixture as a solid or plastic phase distinct from the solvent. Chemical differences are also significant, including a high fraction of aromatic carbon (over 70%), a high content of organic oxygen, and a low concentration of organic sulfur. Consequently, the thermal chemistry of coal liquefaction is dominated by aromatic structures linked by 1- and 2-carbon or ether bridges.[21] During cracking of petroleum residues, a portion of the feed tends to form carbon-rich hydrogen-deficient coke which is a highly aromatic insoluble solid. In terms of physical state and molecular weight, coal liquefaction bears some striking similarities to this coking process, except operating in the reverse direction.

The fourth chemical process that has some common features with cracking of residues is formation of soot during oxidative pyrolysis and combustion of vapor

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fuels. As in the case of coal, the chemistry of oxygen compounds is significant and unrelated to residue cracking. The similarity lies in the formation of polynuclear aromatic hydrocarbons which agglomerate to form soot particles. Both soot formation and coking are disproportionation processes, where most of the feed reacts to form lower molecular weight species, while a portion reacts to give a much higher molecular weight material than the initial feed. The chemistry of formation of polynuclear aromatic hydrocarbons (PAHs) in sooting flames offers some possible insight into coking reactions.

Thermodynamics of Cracking

Cracking of residues at 410–550 °C is thermodynamically favored, otherwise the reactions would not occur. Due to the complexity of residue materials, detailed thermodynamic analysis is not possible, but a very simple analysis will illustrate the importance of disproportionation products. If we consider the most studied industrial cracking reaction, the conversion of ethane to ethylene:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (1)$$

the free energy of reaction is $\Delta G^{\circ}_{R,298} = 101.0$ kJ/mol;[22] therefore, the reaction cannot occur at low temperatures. At the high temperatures of a cracking furnace (ca. 1000 K), the reaction is much more favorable so that $\Delta G^{\circ}_{R,1000} = 9.102$ kJ/mol and significant conversion of ethane to ethylene will occur at equilibrium. Surprisingly, an alternate disproportionation reaction is much more favorable:

$$C_2H_6 \rightarrow CH_4 + H_2 + C(s) \qquad (2)$$

with a free energy of reaction of $\Delta G^{\circ}_{R,298} = -50.80$ kJ/mol.[22] This reaction is not kinetically favorable, even at high temperature, but this simple observation does help to underscore one important point about all cracking processes: a portion of the feed tends to form a higher molecular weight carbon-rich material (graphite in the case of eq 2). In ethane cracking, a small portion of the products are aromatic compounds of 6 or more carbons, in pyrolysis in a sooty flame PAHs can form from methane, and in residue cracking coke tends to form.

Polymerization provides another view of this tendency to disproportionation. The growth of a polymer chain by monomer addition can be written:

$$M + M^{\bullet} \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} M{-}M^{\bullet} \qquad (3)$$

free-radical polymerization is carried out at low temperatures, typically below 150 °C. At higher temperatures, the reverse of polymerization (i.e., cracking) becomes more important. At the ceiling temperature of a free-radical polymerization, the rate of polymerization of monomer and the rate of cracking the chain are equal. Using thermochemical data from Huyser[23] and heat capacities from Benson,[24] the ceiling temperature for ethylene addition to an ethyl radical is approximately 440 °C, and 346 °C for styrene addition. At the temperatures of commercial residue processing, therefore, some extent of polymerization of olefins to higher boiling species is possible depending on the olefin structure. Both thermodynamics and kinetics are favorable for such reactions.

Table 1. Bond Dissociation Energies (Data of McMillen and Golden[25])

chemical bond	representative bond	energy, kJ/mol
C–C (aliphatic)	$C_2H_5{-}nC_3H_7$	344 ± 4
C–H primary	$C_2H_5{-}H$	411 ± 4
C–H secondary	$iC_3H_7{-}H$	398 ± 4
C–H aromatic	$C_6H_5{-}H$	464 ± 8
C–S	$CH_3S{-}C_2H_5$	307 ± 8
C–N	$C_2H_5{-}NH_2$	342 ± 8
C–O	$C_2H_5O{-}C_2H_5$	344 ± 4

Importance of Chain Reactions in Liquid-Phase Cracking

Although free-radical chain reactions are the basis for gas-phase cracking reactions, the importance of chain reactions has often been ignored in the literature on conversion of petroleum and bitumen residue fractions. Thermodynamics and kinetics dictate, however, that chain reactions are favored for thermal cracking reactions. The minimum energy required to break a stable chemical bond is high, as illustrated by the bond dissociation energies in Table 1. The observed activation energies for cracking reactions are considerably lower, both for pure compounds and for residues. For example, Olmstead and Freund[26] determined an activation energy for cracking Arab Heavy and Cold Lake residues of 212.8–216.7 kJ/mol. This value is well below even the weakest bond given in Table 1. The reaction scheme in Figure 1 provides the simple answer. The initiation step to form the radicals can require a high activation energy, but once formed the radicals can propagate through many scission and hydrogen abstraction steps before terminating. These steps have much lower activation energies, therefore, the overall reaction becomes energetically feasible. If the termination step for the chain reaction is

$$M^{\bullet} + R^{\bullet} \xrightarrow{k_4} \text{Products} \qquad (4)$$

and we assume that the reaction chain is long, then the rate of disappearance of the parent compound is

$$-\frac{dM}{dt} = \left(\frac{k_1 k_2 k_3}{k_4}\right)^{1/2} M \qquad (5)$$

and the overall activation energy is

$$E_a = {}^{1}/_{2}(E_{a1} + E_{a2} + E_{a3} - E_{a4}) \qquad (6)$$

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Table 2. Homolytic Thermal Cracking of 1,5-Diphenylpentane[a]

T, °C	$t_{1/2}$, h
400	1.66E + 05
430	1.57E + 04
530	22

[a] Rate constants calculated from preexponential factor of $A = 3.16 \times 10^{15}$, activation energy 309.4 kJ/mol, after Poutsma.[31]

The high activation energy of the initiation step (E_{a1}) has a much smaller impact on the overall reaction if a chain reaction takes place.

Chain reactions have been demonstrated for alkanes, alkylaromatics, and cyclic saturated compounds, both in the vapor phase and in the liquid phase.[14,16,17,27−30] A review by Poutsma[31] showed that chain reactions were significant in cracking of a wide range of aromatic compounds with 2 or more alkyl carbons attached. Nonchain reactions were significant only for cracking of unsubstituted and methyl-substituted aromatics. One significant difference between chain and nonchain cracking reactions is rate of reaction. A high energy barrier gives slow rates, as illustrated in Table 2. If every bond scission requires homolytic breakage, without chain reaction, then the reactions are too slow to be of any significance in a commercial process. As indicated in eq 6, the addition of lower-energy propagation steps gives a significant reduction in the energy required, thereby increasing the rate.

In contrast to cracking in the gas phase, a liquid medium presents a much higher density of molecules for reaction with a free radical. For example, in cracking *n*-hexadecane at 410 °C the concentration of hydrogen atoms available for abstraction in the saturated liquid increases by 2 orders of magnitude compared to the gas phase at 101 kPa, therefore, hydrogen abstraction is much faster than in gas-phase cracking. This change in the propagation step shifts the selectivity of the cracked products from a high yield of olefins in vapor-phase cracking (β-scission dominant) to an equal yield of olefins and alkanes in liquid phase.[27,28,32] This trend is illustrated by the results of Wu et al.[33] on thermal cracking of *n*-hexadecane in the liquid phase and in the gas phase. As illustrated in Figure 2, at 375 °C and 2 h reaction the products shift from nearly equal-molar yields of alkanes and olefins from C_3−C_{13} in liquid-phase cracking, to high yields of light ends and olefins in vapor-phase cracking. Wu et al.[33] found that the same reaction steps and the same kinetic parameters were applicable to both vapor- and liquid-phase reactions, but that the overall reaction rate constant for conversion of n-C_{16} at 375 °C decreased from 1.15×10^{-2} h^{-1} in liquid phase to 8.6×10^{-3} h^{-1} in gas phase. The somewhat higher rate of conversion in the liquid phase was consistent with the formation of higher molecular weight species by addition reactions. The relatively small differences in the rate constants for conversion from Wu et al.[33] emphasize the fundamental similarities between cracking in the vapor phase, as in steam cracking to form olefins, and cracking in the liquid phase as in residue conversion.

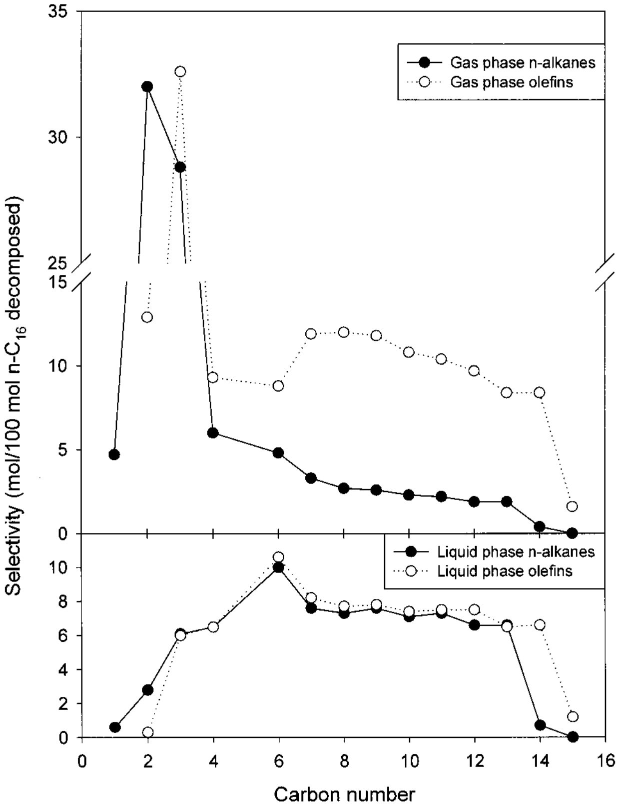

Figure 2. Yields of alkane and olefin products from cracking of *n*-hexadecane in the gas and liquid phases at 375 °C for 2 h (data from Wu et al.[33]).

Initiation: $$R\text{-}R' \xrightarrow{k_{in}} R^{\bullet} + R'^{\bullet} \qquad (1)$$

Propagation:

Hydrogen abstraction $$\beta_j^{\bullet} + R_jH \xrightarrow{k_{ij}} \beta_jH + R_j^{\bullet} \qquad (2)$$

β-Scission $$R^{\bullet}\text{-C-C-}\beta_j \xrightarrow{k_i} R\text{-C=C} + \beta_j^{\bullet} \qquad (3)$$

Radical Addition $$R_i^{\bullet} + \text{C=C-}R_k \xrightarrow{k_a} R_i\text{-C-C}^{\bullet}\text{-}R_k \qquad (4)$$

Termination: $$R_i^{\bullet} + R_j^{\bullet} \xrightarrow{k_t} R_i\text{-}R_j \qquad (5)$$

Figure 3. LaMarca-Libanti-Klein-Cronauer (LLKC) free-radical chain reaction mechanism for liquid-phase cracking (after LaMarca et al.[34]). Hydrogen atoms are omitted for clarity, and the radical−hydrogen transfer reaction is omitted.

Just as in pyrolysis of *n*-alkanes and alkyl-substituted species, the mechanism for coal liquefaction can also be written as a free-radical chain reaction,[34] as illustrated in modified form in Figure 3. In this scheme, R, γ, and X represent portions of the coal macromolecule, while β represents solvent components. The work of LaMarca et al.[34] is one of the few examples of mechanisms for liquid-phase cracking reactions of complex feeds that incorporate chain reactions, although several authors have suggested that alkylaromatic materials such as heavy oils undergo cracking via free-radical chain

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reactions.[6,9,35] LaMarca et al.[34] emphasized the importance of extending the chain reaction as much as possible to maximize conversion of the coal material, by maximizing the initiation and propagation steps (with the exception of radical addition) and minimizing the termination step. A second crucial reaction that they suggested was the addition of radicals to olefins. Every reaction shown in Figure 3 has been observed in reactions of pure compounds or mixtures of pure compounds; therefore, the LaMarca-Libanati-Klein-Cronauer (LLKC) mechanism meets the criterion of verification of the chemical reaction steps, and it is fully consistent with the characteristics of gas-phase cracking of hydrocarbons (Figure 1). Consequently, we can adopt the LLKC mechanism as given in Figure 3 as a consistent basis for understanding the liquid-phase cracking of petroleum and bitumen residues.

The LLKC mechanism directly contradicts one of the standard claims in past attempts at analyzing cracking reactions of residues and coal: that free radicals are harmful, and that quenching or "capping" of free radicals is both desirable and feasible. This hypothesis was first proposed by Curran et al.[36] to explain the benefits of liquefying coal in donor solvents such as tetralin. They proposed a two-step mechanism for thermal cracking of coal: homolytic scission of bonds in the coal, followed by abstraction of hydrogen from the donor solvent. This hydrogen abstraction successively converted tetralin to 4 moles of stabilized or capped radicals and one mole of naphthalene. By "capping" radicals, Curran et al.[36] claimed that polymerization was prevented and the yield of liquids was thereby increased. The key weakness of this hypothesis is that the rate-controlling step in conversion becomes the unfavorable homolytic scission of a bond, rather than much more favorable propagation steps as in Figure 3. As illustrated in Table 2, such a process would not proceed at the rates that are actually observed.

The importance of free-radical chain reactions in cracking of vacuum residue was tested directly by Blanchard and Gray.[35] Athabasca residue was dissolved in 1-methylnaphalene at a molar concentration of ca. 1.2%. Following the LLKC mechanism, radicals from cracking of the residue would abstract hydrogen from 1-methylnaphthalene, giving relatively stable benzylic radicals. This shift in the chain carrier would have two measurable effects: first a decrease in the rate of cracking of the residue and second the introduction of detectable termination steps due to recombination of the methyl−naphthalene radical carriers. When undiluted Athabasca residue was reacted at 400 °C under 13.8 MPa hydrogen pressure for 30 min in an autoclave, the conversion of the 524+ °C fraction averaged 48.6%. When diluted in 1-methylnaphthalene, the conversion dropped to a mean of 35.7%. At the same time, the concentration of di-naphthyl species due to termination reactions of the methlynaphthyl radicals increased by a factor of 3.6, in comparison to blank experiments with 1-methylnaphthalene and no residue. These results followed the general predictions of the LLKC mechanism for chain reactions, and indicated that cracking of residue was not simply due to homolytic scission reactions followed by radical stabilization or recombination.

Direct experimental tests of the ability of donor solvents such as tetralin to quench radicals have had mixed results. In situ electron spin resonance (ESR) spectrometry of coal during pyrolysis and liquefaction reactions showed a significant increase in total radical concentration with time, but Sprecher and Retcofsky[37] suggested that the active radicals involved in cracking were too transitory to be observed. Addition of the hydrogen donor solvent 9,10-dihydrophenanthrene reduced the total radical concentration by a factor of 2, compared to reaction without solvent or reaction with phenanthrene. Given that the active radicals were not observed in this experiment, the hydrogen donor solvent had a definite interaction with the precursors to stable radicals. Other in situ ESR spectrometry experiments by Petrakis and Grandy[38] found that out of a group of six different coals, only half gave a change in radical concentration when reacted in tetralin with hydrogen gas in comparison to naphthalene with hydrogen gas at 400−480 °C. Radical quenching, even of stable radicals that accumulate during cracking, was clearly not a general phenomenon.

The fundamental difficulty in measuring radical concentrations in situ is the high background concentration of stable radicals, in the range of $10^{18}-10^{19}$ spins/g for both coals[37,38] and for asphaltenes from heavy oil and bitumen.[39] During reaction, these materials tend to increase the concentration of radicals due to the formation of stable species. Acevedo et al.[39] suggested that the stable radicals in asphaltenes from crude oil were due to highly aromatic radicals, which gave significant delocalization of the radical center. They further suggested that the association of the asphaltene molecules in the oil prevented reaction of these radicals with oxygen or other components with abstractable hydrogen.

Solvent can have important roles during degradation of coal macromolecules by providing abstractable hydrogen to radicals on the large coal molecules, which helps to prevent polymerization and condensation reactions.[40] The mobile solvent radicals can then initiate new reactions elsewhere in the coal matrix. This "relocation" of radicals by mobile solvent within the coal matrix is likely responsible for the reduction in stable radical formation observed by Sprecher and Retcofsky[37] due to addition of hydrogen donor solvent. This interaction would account for the benefits of donor solvents observed by Curran et al.,[36] without eliminating the radical chain reactions under the LLKC mechanism.

Significance of Olefin Formation

By the basic nature of a free-radical chain process, the concentration of active radicals remains low, while the amount of product accumulates rapidly. In the case of polymerization, the polymer chains accumulate. In

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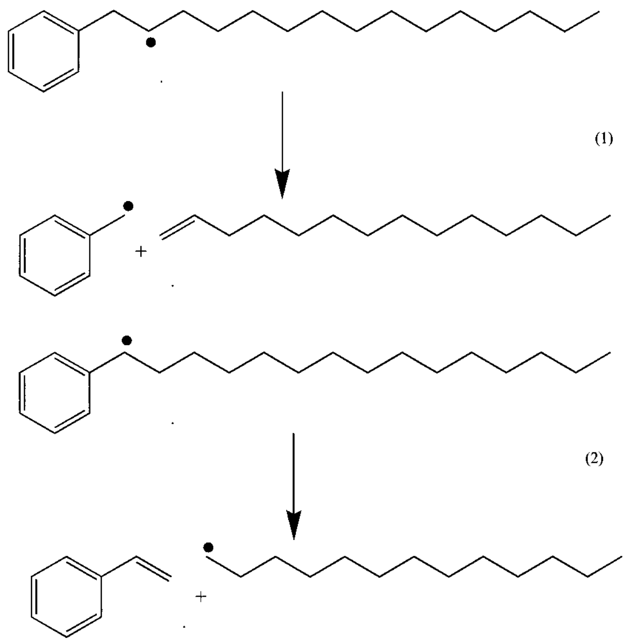

Figure 4. Favored pathways for cracking of alkyl benzene: *n*-pentadecyl benzene.[16]

the case of cracking, a mixture of saturated and unsaturated cracked species will accumulate. As indicated in Figure 3, the nature of the unsaturated species depends on the propagation step. For every mol of bonds broken by β-scission (reaction 3), the chain reaction produces one mole of saturated product and one mole of unsaturated olefin products. The specific structures of these compounds depend on the radical that has undergone β-scission.

The most abundant products from β-scission usually result from the reaction pathway that either begins from the most stable radical or the reaction pathway that forms the most stable product radical. For example, in cracking of an alkyl-aromatic such as *n*-pentadecylbenzene (n-C_{15} benzene), the most abundant products of cracking are toluene and *n*-tetradecene due to the stability of the benzyl radical (reaction 1 of Figure 4). The second most abundant products derive from the most stable parent radical (reaction 2 of Figure 4), giving styrene and *n*-tridecylbenzene.[16] Similar patterns of selectivity were observed for alkyl-cyclohexanes.[17] From these studies, the olefins from cracking of residue components would be of two main types: aliphatic olefins from rings and side chains and conjugated olefins of the styrene type. The α-olefins from cracking, as in Figure 4, would also undergo isomerization to give internal olefins.

Evidence from the cracking of side chains on larger fused-ring aromatics indicated a very different pattern of reaction. Pyrolysis of 1-dodecylpyrene at high conversion gave mainly pyrene and dodecane as products,[29] which would require the scission of the strong bond between the pyrene and its n-C_{12} side chain. Olefins were formed in lower yields than from pyrolysis of alkyl benzenes. Savage et al.[29] suggested that the radical–hydrogen transfer mechanism of Malhotra and McMillan[41] was responsible for this cleavage, wherein a hydrogen β to a radical is transferred to an unsaturated carbon. Subsequently, studies of the radical–hydrogen transfer reaction using three different molecular orbital calculation methods provided a consensus that this reaction had an energy barrier ca. 50 kJ/mol higher than the alternative hydrogen abstraction reaction.[42–44] These results support the suggestion by Camaioni et al.[45] that combinations of the other elementary steps account for the apparent radical–hydrogen transfer reaction in hydrocarbon mixtures.

The difficulty in the experiments of Savage et al.[29] was the lack of a hydrogen donor compound to account for the low concentration of olefins. Along with formation of products that were too rich in hydrogen, the cracking reaction also produced insoluble product which could not be analyzed. Freund et al.[46] used a similar model compound, 1,20-dipyrenyl eicosane, in an open reactor system to show that the hydrogen was abstracted from the alkyl chain group in the β-position, forming an internal olefin. In the open reactor, this material was detected in the products, whereas in the closed reactor of Savage et al.,[29] the analogous olefins from dodecyl pyrene apparently underwent significant polymerization. For example, the lost material accounted for 40–85% of the total amount of 1-dodecylpyrene converted at 425 °C, depending on the time of reaction. This observation of formation of “coke” from a simple compound, coupled with the identification of the unsaturated intermediates by Freund et al.,[46] further supports the hypothesis that olefins are crucial compounds in coke formation.

Once the olefins form and accumulate, a number of reactions are possible, including further cracking, hydrogenation by exchanging hydrogen with other components in the mixture, and addition to free radicals, as in free-radical polymerization. The LLKC mechanism (Figure 3) includes the addition of a radical to an olefin, which is the reverse of β-scission. Although the scission reaction is favored, for example for styrene above 346 °C,[23] the addition reactions are still significant.

Experiments by Khorasheh and Gray[30,47] provided two examples of addition of olefins to free radicals. Cracking of *n*-hexadecane in the liquid phase gave the expected distribution of C_2–C_{14} alkanes and olefins, but at high conversion levels the yields of olefins were suppressed. Instead, the product mixture showed a series of branched alkanes with carbon numbers ranging from C_{17} to C_{31} as illustrated in Figure 5. These products formed from the addition of an olefin to a *n*-hexadecyl radical, therefore, this reaction accelerated as the olefins accumulated in the reaction mixture. Wu et al.[33] also observed addition products in the thermal cracking of *n*-hexadecane, but only when the reactions were carried out in the liquid phase. These bimolecular addition reactions were not favorable at the low densities of vapor-phase cracking.

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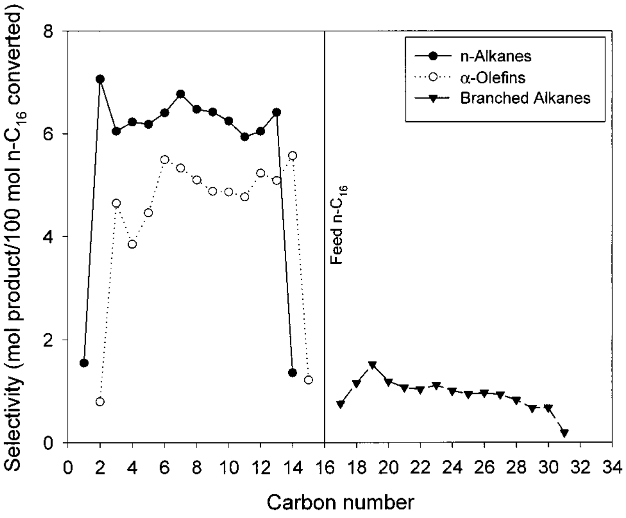


Figure 5. Yield of products from cracking of *n*-hexadecane in liquid phase at 434 °C, 6.61% conversion (Data of Khorasheh and Gray[30]).

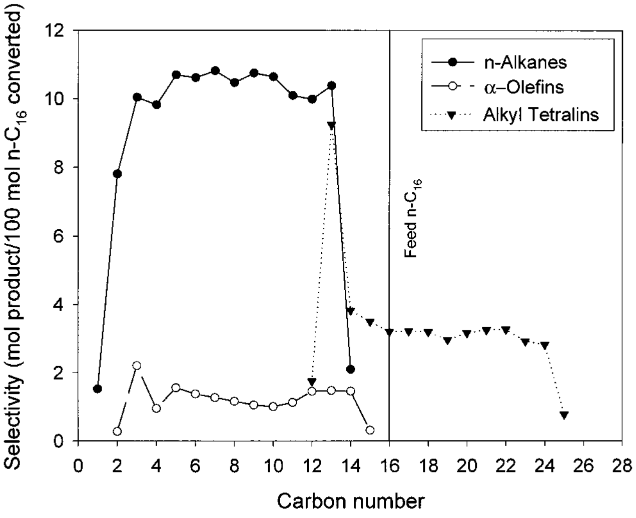
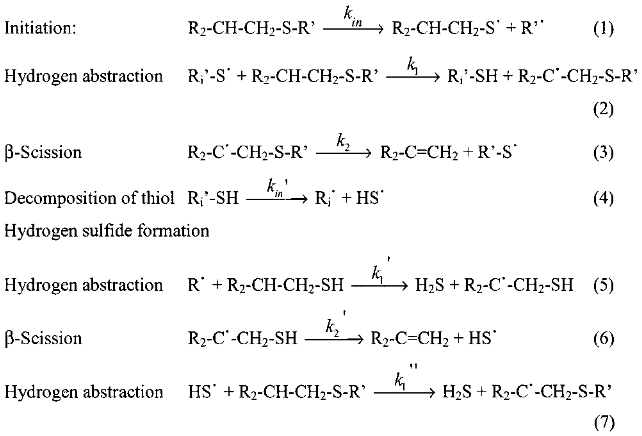


Figure 6. Yield of products from cracking of a liquid mixture of 3 mol % *n*-hexadecane in tetralin at 420 °C, 7.12% conversion (data of Khorasheh and Gray[47]).

When *n*-hexadecane and tetralin were reacted together, the addition reactions of olefins were even more significant. As illustrated in Figure 6, the yield of olefins was suppressed significantly, and a series of alkyltetralins were a major class of products. The rate of cracking of *n*-hexadecane in tetralin was approximately one-half of the rate observed for the pure compound. Both observations, the addition products and the suppressed rate, were consistent with the formation of benzylic type tetralyl radicals by the abstraction of an α-hydrogen from tetralin. This favorable abstraction reaction would reduce the rate of abstraction from *n*-hexadecane, thereby suppressing the rate of cracking. Olefin addition to these tetralyl radicals gave the observed alkyl-tetralin products. This chain transfer process was consistent with the analysis of LaMarca et al.[34] Contrary to the radical capping hypothesis of Curran et al.,[36] the *n*-alkyl radicals were not quenched; they were transferred to tetralin as an alternate chain carrier.

The work of Khorasheh and Gray[30,47] showed that olefins undergo addition reactions in the liquid phase


Initiation: $R_2\text{-CH-CH}_2\text{-S-R'} \xrightarrow{k_{in}} R_2\text{-CH-CH}_2\text{-S}^{\bullet} + R'^{\bullet}$ (1)

Hydrogen abstraction $R_i'\text{-S}^{\bullet} + R_2\text{-CH-CH}_2\text{-S-R'} \xrightarrow{k_1} R_i'\text{-SH} + R_2\text{-C}^{\bullet}\text{-CH}_2\text{-S-R'}$ (2)

β-Scission $R_2\text{-C}^{\bullet}\text{-CH}_2\text{-S-R'} \xrightarrow{k_2} R_2\text{-C=CH}_2 + R'\text{-S}^{\bullet}$ (3)

Decomposition of thiol $R_i'\text{-SH} \xrightarrow{k_{in}'} R_i^{\bullet} + HS^{\bullet}$ (4)

Hydrogen sulfide formation

Hydrogen abstraction $R^{\bullet} + R_2\text{-CH-CH}_2\text{-SH} \xrightarrow{k_1'} H_2S + R_2\text{-C}^{\bullet}\text{-CH}_2\text{-SH}$ (5)

β-Scission $R_2\text{-C}^{\bullet}\text{-CH}_2\text{-SH} \xrightarrow{k_2'} R_2\text{-C=CH}_2 + HS^{\bullet}$ (6)

Hydrogen abstraction $HS^{\bullet} + R_2\text{-CH-CH}_2\text{-S-R'} \xrightarrow{k_1''} H_2S + R_2\text{-C}^{\bullet}\text{-CH}_2\text{-S-R'}$ (7)

Figure 7. Possible reaction pathways for alkyl sulfur compounds in residues.

at the temperatures where petroleum and bitumen residue conversion processes operate. These addition products of the olefins would in turn be subject to cracking. By continuing these addition reactions by further polymerization, olefins have the potential to build still higher molecular weight material, or coke. This possibility will be discussed in a later section on coke formation.

Sulfur Compounds

The preceding examples have tended to focus on the reactions of hydrocarbons, but the thermal reaction chemistry of the thioether sulfur in residue fractions are also important. Alkyl sulfur compounds, in rings and chains, have been identified in crude oils.[7] These compounds have weaker bonds than hydrocarbons (Table 1), and are likely candidates for initiation reactions. Experimental studies of asphaltene cracking have clearly shown that hydrogen sulfide is a favored product at low temperature.[48−50] Bond energies of order 300−320 kJ/mol (Table 1; Thomas et al.[51]) make initiation favorable at temperatures of 350−400 °C, leading to free-radical chain reactions as illustrated in Figure 7. Chain reactions of sulfides by β-scission to give thiol and olefins are well-known, as are the reverse addition reactions.[23] Evolution of hydrogen sulfide is also consistent with chain reactions. Thomas et al.[51] suggest a second initiation step as shown in reaction 4, Figure 7, but this has a bond dissociation energy of ca. 310 kJ/mol. A more likely pathway is a cycle of hydrogen abstraction and β-scission, as in reactions 5−7 of Figure 7. Regardless of the exact mechanism of hydrogen sulfide formation, alkyl sulfides are likely initiators of free-radical chain reactions in residues. Indeed, Thomas et al.[51] took this approach one step further by adding sulfur compounds and hydrogen donors during mild thermal cracking, to initiate cracking and to hydrogenate intermediates.

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Mechanism of Coke Formation

The formation of insoluble carbonaceous material during upgrading processes is a key issue for both yield of liquid products from thermal cracking and for operability of different types of reactors. The accumulated evidence suggests that coke formation is preceded by phase separation in the liquid phase, driven by cracking reactions that leave behind more aromatic components than in the initial oil mixture. When these components reach a critical concentration in the reaction mixture, they separate from the main liquid phase and coke formation follows rapidly.[52] A similar mechanism has been suggested for cracking under high-pressure hydrogen[53] and verified with pure compounds. Shaw et al.[54] demonstrated that the lower solubility of hydrogen in the aromatic phase helped to drive the separation of liquid phases. Evidence from microscopy of coke and other phases formed in the liquid phase supports the phase separation mechanism.[55,56] Once formed, a portion of the toluene-insoluble coke material can then react further to form the nematic mesophase, which is observed under cross polarized light. At short reaction times, solubility in quinoline can distinguish between isotropic material (soluble in quinoline) and insoluble mesophase.[57] On the basis of optical studies and solubility, the coke from petroleum residues often shows a low fraction of mesophase due to factors such as relatively high sulfur and nitrogen content.[57]

Wiehe[52] points out that the formation of toluene-insoluble material is very fast once the phase separation occurs, so that his kinetic model for coking uses an infinite rate constant. Rahmani et al.[58] used a model similar to Wiehe's to describe coke formation from asphaltenes but with a finite rate constant for coke formation. Consistent with Wiehe's observation, they found that the rate of conversion to coke was very high once phase separation occurred. At the molecular level, the formation of coke likely involves polymerization and condensation reactions between aromatic ring groups, leading to an increase in aromatic carbon content with time. These reactions are very difficult to follow because the products are insoluble. Most models and discussion in the literature assume that coke forms by termination reactions between large aromatic radicals,[1,2,52] as follows:

$$\phi_1^{\bullet} + \phi_2^{\bullet} \rightarrow \phi_1 - \phi_2 \tag{7}$$

where ϕ_1 and ϕ_2 are aromatic groups. This type of reaction is thermodynamically feasible, and it would give rise to stable biphenyl-type linkages, but is this reaction sufficient to explain the observed behavior during coking, and is it consistent with other processes that produce highly aromatic condensed products?

When a residue solution undergoes phase separation, according to the Wiehe model, the most aromatic species form a separate phase where they rapidly react to form insoluble coke. Free radicals in an alkyl−aromatic oil mixture are most stable in the benzylic position on monoaromatics and polyaromatics, and even more so in conjugated polycyclic compounds which delocalize the radical center efficiently over a number of carbon atoms.[39] Phase separation, therefore, would immediately remove a large fraction of the radicals from the oil phase. Reaction 7 would then be much more favorable in the separated phase due to the increased local concentration. If reaction 7 is dominant and rapid, the total concentration of radicals in the remainder of the mixture would drop rapidly as soon as phase separation occurs. The combination of a drop in total radicals, and a segregation of the aromatic radicals in the new phase, would significantly reduce the rate of any free-radical chain reactions. The result would be an immediate decrease in the rate of cracking. The experimental data, however, show no change in the rate of volatile evolution during coking,[52] which suggests that reaction 7 is an incomplete mechanism. In addition, in situ ESR measurements on a variety of char and coke formation reactions show that the total concentration of radicals in a mixture tends to increase with time[37,38] due to the formation of stable radicals in an increasingly immobile matrix. If reaction 7 is predominant and rapid, no increase in stable radicals would be observed with time.

Polymers can be stable at high temperatures, for example, polyamides can have melting points as high as 536 °C.[59] A reasonable mechanism for coke formation from hydrocarbons is free-radical chain polymerization, followed by rearrangement to give a more thermally stable product. If we return to the LLKC mechanism, reactions 3 and 4 in Figure 3 are essentially forward and reverse reactions:

$$\mathrm{R}^{\bullet}-\mathrm{C}-\mathrm{C}-\beta_{\mathrm{j}} \underset{k_{\mathrm{a}}}{\overset{k_{\mathrm{i}}}{\rightleftharpoons}} \mathrm{R}-\mathrm{C}=\mathrm{C} + \beta_{\mathrm{j}}^{\bullet} \tag{8}$$

In addition to undergoing β-scission, when the aromatic rings in groups R and β favor rearrangement then the radical can also rearrange to become more stable:

$$\mathrm{R}^{\bullet}-\mathrm{C}-\mathrm{C}-\beta_{\mathrm{j}} \xrightarrow{k_{\mathrm{s}}} \mathrm{R}_{\mathrm{i}}^{\bullet} \tag{9}$$

where the aromatic group in radical $\mathrm{R_i}$ is larger due to the addition and rearrangement reactions. Reaction 9 would require sequential steps of rearrangement followed by loss of hydrogen to give a stable aromatic species, but end the result would be formation of a condensed, more stable, compound with higher molecular weight than the starting reactants. As the size of the radical $\mathrm{R_i}$ grows, the resonance stabilization of the radical center over multiple carbon atoms would increase, giving a less reactive radical species and contributing to the accumulation of spins noted in in situ ESR studies.

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Studies of PAH formation in sooting flames suggest that free-radical reactions can sequentially build larger aromatics by free-radical addition reactions, followed by unimolecular rearrangements into more stable structures.[60−62] At the high temperatures of such flames, addition of species such as acetylene onto cyclic compounds are important steps in building large PAH compounds such as coronene and fullerenes. In steam cracking of naphtha and gas oil, cyclization of diolefins such as butadiene is a significant retrograde reaction. Diolefins undergo rapid cyclization and aromatization at temperatures characteristics of residue cracking.[63]

A second mechanism for formation of stable toluene-insoluble material by reaction 8 is intermolecular addition reactions. If a portion of a molecule that is already attached by one bond undergoes intermolecular addition, as in reaction 8, then the resulting double-bonded molecular fragment will be retained much more strongly in the liquid phase or coke material. This principal was illustrated by Solomon et al.,[64] who considered pyrolysis of cross-linked networks of aromatic cores. Aromatic groups that were linked by more than one bond to a larger molecule or matrix were much less likely to evolve as products of thermal reactions.

Role of Hydrogen Donors

Despite the lack of evidence for the radical capping hypothesis of Curran et al.,[36] hydrogen donors are extremely important in hydrogen transfer reactions and the benefit of donor compounds in petroleum residue conversion has been recognized for many years.[65,66] The transfer of hydrogen from hydroaromatic species such as tetralin and 9,10-dihydrophenanthrene is extremely important in helping to control coking reactions. Rather than eliminating radicals, hydrogenation of olefins is a crucial benefit of hydrogen donors. Hydrogen donors react very readily with olefins; for example, Ruchardt et al.[67] observed almost quantitative hydrogenation of α-methyl styrene to cumene by 9,10-dihydroanthracene. This behavior was common to a range of donor compounds and hydrogen acceptors, and subsequently Morgenthaler and Ruchardt[68] showed that PAH donors with weak C−H bonds catalyze the hydrogen transfer from 9,10-dihydroanthracene at temperatures as low as 200 °C. The catalytic compounds, such as dibenzoanthracenes and benzopyrene, could be present in liquid-phase cracking of petroleum residues and bitumens. The benefit of hydrogenation of olefins is clear in Figure 3 and in eqs (8) and (9). Removal of the olefins eliminates a pathway for polymerization and coke formation, thereby suppressing the yield of coke.

Role of Catalysts and Additives

A number of processes for conversion of residues use a combination of hydrogen gas and either dispersed metal compounds of supported transition metals as catalysts in order to enhance residue conversion and suppress coke yield. The role of these catalysts is to transfer hydrogen from the vapor phase into the liquid mixture. Given the complexity of residue materials, such catalytic reactions can be promoted not only by the added catalysts, by also solids in the oil and by the walls of reactor vessels. The metal walls of reactors give appreciable catalytic activity in small-scale experiments.[69] When catalysis is rigorously excluded, as in a quartz-lined flow reactor, the activity of hydrogen gas is rather low.[70]

While the importance of hydrogen transfer by the catalyst to heavy components has long been recognized as a key step in suppressing coke formation,[71] the nature of the reactions has been less clear. From numerous studies of pure compounds, transition metal sulfide catalysts plus hydrogen gas can hydrogenate olefins, partially hydrogenate polynuclear aromatic hydrocarbons, remove sulfur, vanadium and nickel from the oil, and remove nitrogen. These catalytic reactions are superimposed on the main conversion process of thermal cracking[1,2,71−73] giving enhanced selectivity for liquid products. Iron sulfides are capable of olefin and PAH partial hydrogenation.[74] Catalysts consisting of Ni/Mo sulfides supported on alumina, silica, or carbon are effective for these reactions plus hydrodesulfurization and removal of vanadium and nickel.[71,72,75] Removal of nitrogen compounds tends to be inhibited by the presence of high nitrogen concentrations in residues. The hydrogenation and desulfurization reactions reduce the boiling point of the residue components, allowing them to distill with the heavy gas oil fraction and giving a boost in apparent residue conversion.[9]

Following the “radical capping” hypothesis of Curran et al.,[36] a number of authors claimed that the free radicals formed by thermal cracking reactions would be hydrogenated by transition metal catalysts.[1,2,76,77] Unfortunately, this widespread and commonly held idea seems to have no basis in chemistry, because such reactions have not been demonstrated in controlled experiments with defined components.

Examination of the literature on heterogeneous catalysis quickly shows that catalyst surfaces lower the energy barrier to the creation of unstable species such

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Initiation: $$\text{R-R'} \xrightarrow{k_{in}} \text{R}^{\bullet} + \text{R'}^{\bullet} \qquad (1)$$

Propagation:

Hydrogen abstraction $$\beta_j^{\bullet} + \text{R}_j\text{H} \xrightarrow{k_{ij}} \beta_j\text{H} + \text{R}_j^{\bullet} \qquad (2)$$

β-Scission $$\text{R}^{\bullet}\text{-C-C-}\beta_j \xrightarrow{k_i} \text{R-C=C} + \beta_j^{\bullet} \qquad (3)$$

Radical addition $$\text{R}_i^{\bullet} + \text{C=C-R}_k \xrightarrow{k_a} \text{R}_i\text{-C-C}^{\bullet}\text{-R}_k \qquad (4)$$

Radical rearrangement $$\text{R}^{\bullet}\text{-C-C-}\beta_j \xrightarrow{k_s} \text{R}_i^{\bullet} \qquad (5)$$

Termination: $$\text{R}_i^{\bullet} + \text{R}_j^{\bullet} \xrightarrow{k_t} \text{R}_i\text{-R}_j \qquad (6)$$

Olefin removal

Donor solvent $$\text{R-C=C} + \text{R'H}_2 \xrightarrow{k_d} \text{R-C-C} + \text{R'} \qquad (7)$$

Catalytic $$\text{R-C=C} + \text{H}_2 \xrightarrow{k_h} \text{R-C-C} \qquad (8)$$

Aromatic hydrogenation $$\text{R'} + \text{H}_2 \xrightarrow{k_a} \text{R'H}_2 \qquad (9)$$

Figure 8. Extended chain reaction mechanism for liquid-phase cracking, including catalytic reactions. Hydrogen atoms are omitted for clarity. Initiation (1) and aromatic hydrogenation (9) reactions also include sulfur compounds.

as free radicals. For example, Carley et al.[78] showed that the hydrogenation of ethylene on palladium proceeded by chemisorption of hydrogen to give hydrogen atoms and adsorption of the ethylene to the metal surface. Surface reaction produced an ethyl radical on the surface of the catalyst, which either reacted with a hydrogen atom to give ethane or polymerized with ethylene to form coke on the catalyst surface (i.e., reactions 8 and 9). The hydrogen spillover from the active palladium onto the alumina support served to generate radicals which were trapped and measured by ESR methods. As in thermal cracking, the formation of free radicals was a necessary intermediate step toward the desired reaction. The results of Carley et al.[78] suggest that hydrogen atoms from catalytic centers could react with radicals generated by homogeneous cracking reactions, but there is no evidence that these reactions would be selective enough to be significant in comparison to other catalytic reactions.

The other arguments against the hypothesis of radical capping by catalytic hydrogenation are identical to the arguments against radical capping by hydrogen donors presented earlier, therefore, these points will not be repeated here. In the context of the LLKC mechanism and reactions 8 and 9, catalysts have two important roles which are based on simple chemistry: hydrogenation of olefins to give saturates and partial hydrogenation of PAHs to give hydrogen donors. Both reactions help to control olefin concentrations, both directly and by enhancing donor solvent hydrogenation of olefins.[67,68]

Implications for Coking and Hydroconversion of Residues

Figure 8 gives the proposed mechanistic framework for conversion of petroleum and bitumen residues, based on the LLKC model with the explicit addition of coke formation, donor solvent and heterogeneous catalytic reactions, and the removal of the radical−hydrogen transfer step based on more recent work.[42−45] Following the original arguments of LaMarca et al.,[34] we can now use this mechanism to consider how to extend the desirable chain reactions for coking and to suppress the undesirable reactions that give rise to coke formation. An important feature of this model is that the undesirable reactions are based on olefins, which are distinct chemical species that can be measured in reactor product streams. Rather than the paradigm of capping of free radicals, the mechanism proposed in Figure 8 suggests an emphasis on measurable and verifiable control of the concentration of olefins in improving or inventing processes for upgrading of residues.

Coking Processes. Delayed and fluid coking processes produce significant concentrations of light olefins in the cracked gases, including ethylene, propylene, and butenes. The naphtha fraction also contains significant concentrations of olefins and diolefins, and the latter often require special treatment in order to avoid polymerization reactions in downstream hydrotreaters.[79] The olefins in the naphtha are easily determined by gas chromatography or bromine titration. Contrary to popular belief, however, the olefins are not restricted to the coker naphtha fraction, but they are more difficult to quantitate. Kulsrestha et al.[80] used a urea adduction method to measure olefins in the gas oil and kerosene fractions in products from delayed coking. Olefin content dropped slightly from 31% in the light kerosene (107−253 °C) to 26% in the gas oil (228−341 °C). Heavier coker distillates also contain olefins, for example Thiel and Gray[81] used ^{1}H NMR to observe olefins in a vacuum gas oil from fluid coking of Athabasca bitumen.

The implication of the mechanism of Figure 8 for coking processes is that rapid removal of olefins in the cracked products should reduce coke yield and increase the yield of distillable liquids. The yield of liquids from delayed coking is enhanced by reducing the operating pressure in the coke drum, which would increase the rate of removal of cracked products from the liquid pool.[82] A more extreme method of stripping is used in the Eureka process, which uses steam to strip the products from the reacting liquid in a delayed-coker type of operation.[83] Not only does this method reduce the yield of coke by 1% of feed, but it also maintains the coke product in a pumpable liquid form, instead of a solid which must be cut out of the drum. Takatsuka et al.[83] attributed the liquidity of the cracked residue, or pitch, to phase behavior, where the removal of the more volatile material prevents phase separation and cross-linking. The mechanism of Figure 8 offers an alternate explanation, in that stripping of volatiles will reduce the concentration of olefins in the reactor, thereby reducing reactions 4 and 5 that lead to stable cross-links between fragments of cracked residue.

Other experiments lend support to the latter interpretation. Sanford and Xu[84] compared cracking of

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Athabasca in the presence of methane to ethylene, at the same temperature of 400 °C and total pressure of 8.4 MPa for 240 min. Reaction in the presence of methane gave 7.5 wt % of toluene-insoluble coke, while reaction in the presence of ethylene gave 12.9 wt % coke. For comparison, reaction under nitrogen at the same conditions also gave only 7.5% coke. Gray et al.[85] found that the yield of coke was reduced when the liquid side transport resistance to the evolution of products was reduced. They demonstrated this trend by reacting thin films of bitumen, and measuring yield as a function of the film thickness. Both of these experimental results are consistent with the mechanism of Figure 8, which indicates that an increase in olefins will enhance the formation of coke material, while rapid removal of olefins in cracked products will reduce coke formation.

The mechanism of Figure 8 suggests that the yield of liquids from coking will be maximal when the olefins are rapidly removed from the reactor (Reaction 7). Hydrogen donors certainly help to suppress coke formation in visbreaking type cracking processes[65,66] but their role in converting olefins in processes such as delayed coking has not been investigated. The implication of Figure 8 is that monitoring the concentration of olefins in coker distillates would be an effective means of assessing the benefits of process changes.

Catalytic Processes. The key role of the catalyst in aiding thermal cracking reactions (reaction 3, Figure 8) and preventing addition reactions (reaction 4) is to promote direct olefin conversion and partial hydrogenation of PAHs to form donor species. In the case of a dispersed catalyst, such as dispersed molybdenum sulfide or iron sulfide, the hydrogenation of olefins will occur wherever the liquid phase is present. Metal sulfide catalysts on γ-alumina or similar supports do not give uniform catalytic activity wherever the liquid phase is present. Donor reactions will be important wherever thermal reactions occur in the absence of catalyst, for example, in high-temperature separators and at the inlet of catalytic reactors.

The proposed mechanism in Figure 8 for interactions between thermal and catalytic reactions suggests that balanced catalytic activity is highly desirable when the process objective is to maximize cracking to reduce molecular weight. Excessive hydrogenation of aromatics will reduce the effectiveness of donor species. For example, hydrogenation of anthracene to 9,10-dihydroanthracene gives a powerful donor, but further hydrogenation to 1,2,3,4,9,10-hexahydroanthrancene gives a much less effective donor compound. Ironically, such hydrogenation will give apparent residue conversion by virtue of the reduction in boiling point of the hydrogenated products.

The most common difficulty with high-conversion hydroconversion of residues is the formation of sludge. This material seems to be partly a low-temperature phenomenon due to incompatibility, not directly related to phase behavior at reactor conditions because dissolution occurs upon heating.[86] Polymerization reactions (reactions 4 and 5 in Figure 8) could contribute to sludge precipitation by increasing the molecular weight of the aromatic material, which was mainly in excess of 600 molecular weight as determined by GPC in one study,[86] but this possible contributing factor to sludge formation has not been investigated. Multistep hydrogenation and cracking was one effective method of suppressing the formation of sludge precipitates, but this benefit could be due to hydrogenation of aromatic material to prevent subsequent incompatibility after thermal removal of side chains.[87]

In fixed-bed catalytic reactors, the deposition of coke or polymeric material is sometimes observed at the reactor inlet. In some cases, this deposition is due to polymerization of the most reactive diolefins, and it can be controlled by prehydrogenation of the feed at a lower temperature.[79] In this case, hydrogenation at 200−220 °C is able to prevent polymerization at hydrotreater inlet temperatures of ca. 320−350 °C. This type of polymer fouling of hydrotreaters is an interesting example of the interplay between thermal polymerization and catalytic reactions that should also be important in hydroconversion at 400−450 °C. Given the lack of past attention to the behavior of olefins and donor species in hydroconversion, further studies may suggest important methods for improving these process technologies.

Acknowledgment. This research was supported by the NSERC/Syncrude Industrial Research Chair in Advanced Upgrading of Bitumen.

EF010243S

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