GENERAL RESEARCH

Molecular Approach to Understanding Residuum Conversion

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Athabasca bitumen residuum was reacted under nitrogen, hydrogen, or hydrogen in the presence of a residuum hydrotreating catalyst for varying times which produced between 40 and 90% residuum conversion. There was little difference among the relative rates of conversion for the three series. The data suggest that the first 30–40% of residuum conversion mainly involves breaking of labile carbon-to-carbon bonds to produce distillate. It is suggested that additional conversion results from the formation of an aromatic-carbon aliphatic-carbon biradical intermediate, which is formed from hydroaromatic structures. Hydrogen transfer to the aromatic-carbon radical center is sufficient to prevent condensation leading to coke formation. The hydrogen radical produced as part of the hydrogen-transfer process can attack a condensed aromatic center, leading to gas and distillate formation from large aromatic molecules. The initially formed aliphatic-carbon radical can preferentially undergo fragmentation to produce gas and distillate.

Introduction

As the world supply of light crude oil diminishes, more and more attention is being paid to the conversion of petroleum residua into refinery products. In this context, the residuum fraction is considered to be the fraction boiling above 524 °C. Conversion is achieved in one of two ways, either by heating at near atmospheric pressure (coking processes) or by heating at relatively high hydrogen partial pressures (11–14 MPa, hydrocracking processes). The hydrocracking processes are carried out either in the presence of a finely divided metal sulfide additive (Dabkowski et al., 1991) to promote hydrogen transfer and prevent coke formation, or in the presence of a residuum hydrotreating catalyst (Beaton and Bertolacini, 1991) which also prevents coke formation and removes heteroatoms and Conradson carbon residue (CCR) through hydrogenation and hydrogenolysis reactions. These two types of hydrocracking processes have been referred to as slurry-phase hydrocracking and hydrogenolysis hydrocracking, respectively (Sanford, 1991b), since many commercial or near commercial processes are based on variations of these two technologies. A third alternative is to prevent coke formation by use of a hydrogen donor solvent (donor solvent hydrocracking (Heck et al., 1992)).

Hydrocracking technologies are the preferred choice for any new installations over coking technologies because liquid yields are higher (approximately 85% compared to 70% for coking), although a significant proportion of the feed is still converted to gases. In addition, hydrocracking processes all generate a pitch fraction, which is often handled by processing in a coker.

Improvements and/or variations in slurry hydrocracking processes have concentrated on ways to prepare the metal sulfide additive in a finely divided form (Dabkowski et al., 1991), usually involving the use of different precursors, sometimes as an oil-soluble additive (Bearden and Aldridge, 1979). The main objective was to find an economical way of preventing coke formation, not to change the chemistry of residuum processing in such a way that higher liquid yields would be achieved. Similarly, hydrogenolysis hydrocracking studies have concentrated on catalyst development for removal of heteroatoms and CCR (Beaton and Bertolacini, 1991), not on the chemistry of hydrocracking. As a result of the approaches taken, processes have been fine-tuned, new processes based on minor variations of old processes have emerged, and some yield advantages have resulted from mechanical changes, but no new technology based on new chemistry has resulted.

Because new processes and significant improvements to existing processes generally precede any real understanding of the chemistry, it is probably safe to conclude that no significant new processes for the upgrading of residuum will now emerge from the normal pathway of using intuition and trial and error, since this approach has been used for many years. The best hope for new, higher yield processes will come from a detailed understanding of the chemistry of residuum processing.

The first step in understanding the chemistry of residuum processing must necessarily be an understanding of the composition of the residuum itself. Two approaches have generally been used, first, to use mainly NMR spectroscopy and elemental analysis to determine average molecular structural parameters (see, for example, Kotlyar et al. (1989), Khorasheh et al. (1987), and Semple et al. (1990)), and second, to use a wide variety of spectroscopic and chemical degradation methods to identify families of compounds present in these very complex mixtures (Mojelsky et al., 1992; Speight, 1989a,b). A traditional SARA (saturates, aromatics, resins, asphaltenes) separation (Reynolds, 1991) often precedes both of the above two characterization approaches.

Although the SARA separation method is based on solubility/polarity of compounds, many studies have been carried out to determine the interconversion of these classes of compounds (Tiwari et al., 1989) and kinetic models have been developed for coking (Mazza and Cormack, 1988a,b), slurry-phase hydrocracking (Koseoglu and Phillips, 1988a,b) and hydrogenolysis hydrocracking (Koseoglu and Phillips, 1988a,b) as if the interconversions were chemical reactions. There is no discernible chemical difference between, for instance, resins and asphaltenes (Strausz, 1989), and their interconversion may or may not involve significant chemical reactions as well as physical changes. It is not surprising that studies on the inter-

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conversions of SARA fractions have not led to any significant insight into the processing of petroleum residua. Attempts to correlate SARA fractions with the processibility of residua have also been unsuccessful (Reynolds, 1991).

The determination of average molecular structures held some promise of providing insight into residuum conversion chemistry. However, the application of the method to the coking of Athabasca bitumen-derived residues (Kirchen et al., 1989), hydrocracking of Alberta bitumens (Gray et al., 1991), visbreaking of residua from conventional oils (Singh et al., 1991), and coking of petroleum residua (Rudnick and Galya, 1991) has provided only limited information and again has not led to a method of predicting processibility of residua.

A promising approach appears to be to use a combination of yield data obtained over a wide range of conversions, together with average molecular structural data and the extensive knowledge of the molecular structures in residua, and to apply this knowledge to coking, hydrocracking, and hydrogenolysis hydrocracking reactions to try to gain some understanding of the complex chemistry of residuum upgrading.

A detailed study of the hydrocracking of Khafji atmospheric residue (300 °C+) with and without a hydrotreating catalyst, at one conversion level, has been reported by Miki et al. (1983). Heck et al. (1992) compared the yields of liquids and coke over a range of severities from Maya vacuum residuum (88.4% >565 °C) under coking, slurry hydrocracking, and donor solvent hydrocracking conditions. Gray et al. (1991, 1992) compared four Alberta residua under hydrogenolysis hydrocracking conditions at three conversion levels and gave a detailed analysis of the products. The main conclusions from these studies were that light oil fractions were formed mainly in thermal reactions and that the source or pressure of hydrogen had no effect on the conversion. The role of catalyst was to supply hydrogen to the heavy oil fraction and prevent coke formation. The catalyst also promoted heteroatom removal and aromatics saturation in the light oil fractions.

In a previous paper (Sanford and Chung, 1991), coking, hydrocracking, and hydrogenolysis hydrocracking reactions on Athabasca bitumen were compared and, from conversions of heteroatoms and residuum, a generalized scheme which showed how the three series may be related was proposed. This scheme provided the starting point for the present paper, in which data will be presented on the same three series, carried out on Athabasca bitumen residuum (524 °C+) in a batch stirred tank reactor but over a much wider range of residuum conversions.

It appeared that a good forum for at least discussing some of the questions which arose was to take the data on product yields and residuum composition and construct a typical molecule that obeyed both the yield and composition data and agreed with the wealth of knowledge currently available (Strausz, 1989a,b) on structural entities and functional groups present in Athabasca bitumen residuum. The next step would be to propose a decomposition pathway for this molecule in coking and hydrocracking reactions, in such a way that the experimentally observed product yields as a function of conversion were observed.

Experimental Section

The apparatus used for the experiments reported here has been described previously (Sanford and Chung, 1991). All experiments were carried out at 400 °C with reaction times varying from 30 to 480 min. The coking experiments were carried out under 11 MPa nitrogen partial pressure. Otherwise, hydrogen was used at the same partial pressure. Enough gas was added to the reactor at room temperature (approximately 5.5 MPa) to give a pressure close to the desired pressure when the temperature reached reaction temperature. As soon as reaction temperature was reached, the pressure was adjusted to reaction pressure and hydrogen was added as needed to maintain the pressure. In the cases where gas generation was greater than gas consumption, the pressure was allowed to increase until the pressure limit of the reactor (34 MPa) was reached. If the reaction pressure approached the pressure limit of the reactor, some gas was bled from the system.

For the hydrogenolysis hydrocracking runs, the catalyst (75 g of a commercial Co–Mo γ-alumina residuum hydrotreating catalyst per 300 g of feed) was predried for 4 h at 107 °C and placed in a stainless steel wire mesh basket immersed below the level of the liquid in the reactor. The catalyst was sulfided by reaction with the feed during the heatup period.

The feed was Athabasca bitumen residuum, prepared by distilling whole bitumen to a 524 °C endpoint. Redistillation of the residuum feed on an analytical D-1160 apparatus gave a composition of 91.0% 524 °C+. The residuum contained 5.5% sulfur, 7047 ppm nitrogen, 81.5% carbon, 9.4% hydrogen, 384 ppm vanadium, 144 ppm nickel, and 24.8% CCR, and 35.5% of the carbon atoms were in aromatic structures as determined by ^{13}C NMR.

After the specified reaction time, the reactor was cooled and a sample of gas removed for analysis. The remainder of the gas was vented and the contents of the reactor slurried in methylene chloride. Any solid which adhered to the reactor walls or internals was carefully scraped off and added to the methylene chloride slurry. The methylene chloride slurry was then filtered through a 45-μm filter followed by a 30-μm filter. The filtrate was then centrifuged for 40 min at 1500 rpm, decanted, and filtered through a 20-μm filter. The solids were combined, dried, and weighed. The solvent was removed from the combined filtrates on a rotary evaporator, and the total liquid was weighed. The feed was also dissolved in methylene chloride and filtered as above to determine the amount of methylene chloride insoluble solids in the feed. During a run with catalyst, part of the feed was deposited on the catalyst in the form of carbonaceous solids, sulfur, and metals. The increase in weight of the catalyst was determined by a loss-on-ignition measurement.

The difference between the amount of feed added and the sum of the solids and liquids recovered and solids on the catalyst was considered to be gases and light hydrocarbons, which boil at or below the boiling point of the solvent (40 °C) and which were generated during the reaction. The total liquid product was distilled, first by spinning band distillation at atmospheric pressure to remove the C-5 to 195 °C fraction, and then by D-1160, first at 20-mm pressure and then at 1-mm pressure to remove the 195–343 °C cut and the 343–524 °C cuts, respectively.

Plots of feed and products as a function of time are provided and discussed in the Results section. The smooth curves which are drawn through the data points do not correspond to any particular model but are an attempt to reasonably represent the progress of the reactions. The curves were drawn such that the mass balance at any given point on the set of curves was within 100 ± 2%. In order to achieve this objective, most of the errors were assigned to the plots of gases generated, since gases were determined

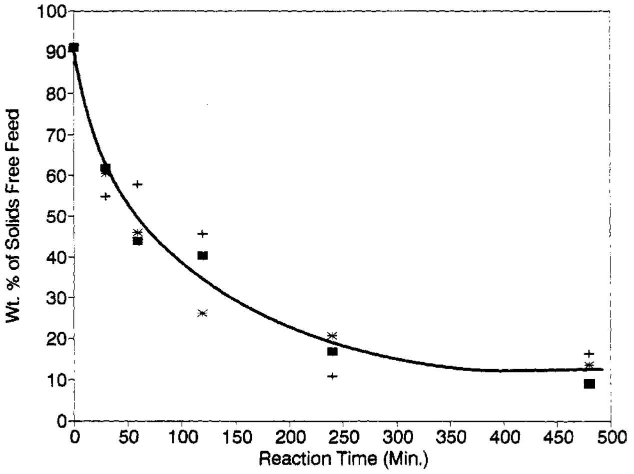

Figure 1. Amount of unreacted residuum as a function of time at 400 °C for reactions carried out under nitrogen, hydrogen, and hydrogen with a residuum hydrotreating catalyst in a batch stirred tank reactor. ■, nitrogen; +, hydrogen; and *, hydrogen and catalyst.

by difference. Nonetheless, the smooth curves do not deviate appreciably from the actual experimental data points.

Results

A. Feed. The feed was found to contain on the average 6.3 g of solids per 300 g of sample, or 2.1 wt %. This amount of solids is equivalent to approximately 1 wt % on a whole bitumen basis and is considered to be normal for Athabasca bitumen produced from a surface mining operation. The solids consisted of approximately 50% mineral matter, of which aluminum, silicon, and iron were the predominant elements. The yield of liquid from the feed after dissolving in methylene chloride was greater than the starting amount, showing that not all of the solvent was removed from this very viscous residuum under the conditions used. Solvent would not necessarily be left in the reaction products since they would be considerably less viscous. The feed also contained approximately 9% gas oil as determined by D-1160 distillation.

B. Residuum Conversion. The amount of residuum remaining after 30, 60, 120, 240, and 480 min at 400 °C is plotted in Figure 1 as a percent of the solids-free feed. Although there is some scatter in the data, it is evident that residuum is not converted to products faster in any one series compared to the others. That is, the presence of hydrogen or hydrogen in the presence of a residuum hydrotreating catalyst did not have any overall measurable effect on residuum conversion, which is expected to be largely a thermal reaction (Sanford, 1991a). Approximately 50% of the residuum was converted in 75 min at the reaction temperature of 400 °C. An additional 175 min was required to achieve 80% conversion and increasing the reaction time to 480 min only resulted in an additional 7% conversion. No attempt was made to determine kinetic parameters since it is very difficult to correct for the relatively long (45 min) heatup period required in a batch reactor.

When the residuum conversion data of Heck et al. (1992) for Maya crude is plotted as a function of equivalent residence time at 427 °C, the runs with hydrogen, a hydrogen donor, and hydrogen with a molybdenum additive all cluster around the same line, similar to the present results. Conversion of Maya residuum under coking conditions was faster than for the corresponding hydrocracking runs.

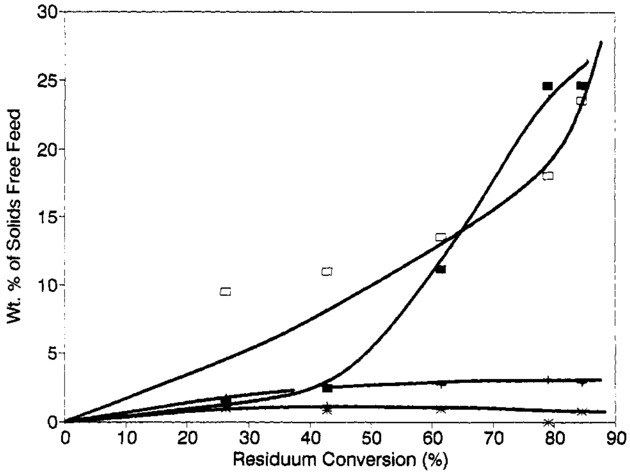

Figure 2. Amount of solids produced as a function of time during residuum conversion at 400 °C for reactions carried out under nitrogen, hydrogen, and hydrogen with a residuum hydrotreating catalyst in a batch stirred tank reactor. Symbols as for Figure 1 except □, solids on catalyst.

C. Solids. Yields of methylene chloride insoluble solids (which were either freely suspended in the reaction product or attached to the reactor internals and were removed by scraping) for the three series are plotted in Figure 2 as a function of residuum conversion. Carbonaceous solids on the catalyst are plotted separately. After correcting for the amount of solids in the feed, the amount of solids produced in the presence of a residuum hydrotreating catalyst, excluding solids on the catalyst, was less than 1%, even after 87% conversion. Solids formation began immediately at the beginning of the reaction and increased gradually. The shape of the curve would indicate that these solids are a primary product which result from initial bond breaking reactions. The low level of solids formed confirms previous conclusions that the catalyst in the presence of hydrogen is very effective in suppressing coke formation in the reaction mixture (Miki et al., 1983; Simpson et al., 1991), and further shows that the catalyst remains effective for suppressing coke formation even after 8 h of use.

Although the amount of solids formed in the reactor in the presence of hydrogen and a hydrotreating catalyst was small, the amount of the feed that was deposited on the catalyst in the form of a methylene chloride insoluble solid was significant, reaching 24% of the feed at 87% conversion. Obviously, hydrogen does not effectively prevent the formation of carbonaceous solids on the catalyst. Despite the fact that a significant proportion of the feed was deposited on the catalyst, there was no significant effect on the relative rate of removal of residuum (Figure 1).

With only hydrogen present, the amount of solids formed in the reaction mixture was slightly larger than without a catalyst, from 1% to 3% and increased slightly with conversion. The amount of solids formed in the coking reaction was nearly linear with conversion after approximately 40% conversion and reached 25 wt % of the feed after 87% conversion. The shape of the curve in this case (asymptotic to the abscissa) indicates that the solids are not a primary product and are formed from secondary reactions. The dramatic difference in the amount of reactor solids formed in the presence of hydrogen compared to nitrogen is apparent in Figure 2 and is similar to the results reported by Heck et al. (1992).

Kirchen et al. (1989) have reported that the amount of coke formed in a semicontinuous laboratory coker unit is

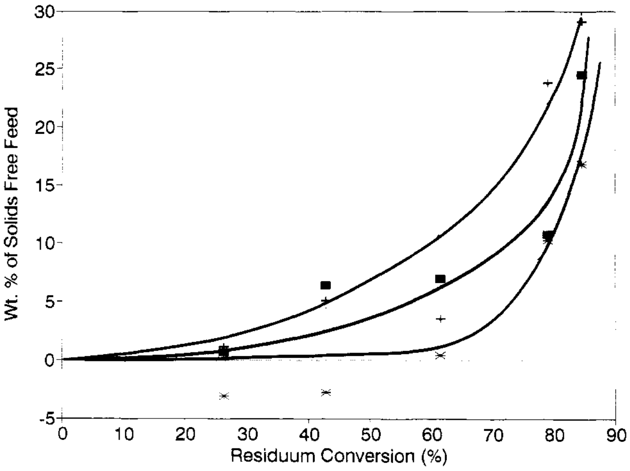

Figure 3. Gases produced as a function of time during residuum conversion at 400 °C for reactions carried out under nitrogen, hydrogen, and hydrogen with a residuum hydrotreating catalyst in a batch stirred tank reactor. Symbols as for Figure 1.

directly related and almost equal to the CCR content of the feed. For this type of "once-through" coking experiment, residuum conversion is approximately 80% (Kirchen, 1992). In the present study, the feed contained 24.8% CCR. Approximately 25% solids were obtained at a residuum conversion of approximately 80% (Figure 2), showing that, at equivalent conversions, the amount of solids produced in the two experiments was similar.

D. Gases. Losses as described in the Experimental Section are plotted as gases (≈C-5–) in Figure 3 for all three series, i.e., coking, hydrocracking, and hydrogenolysis hydrocracking. Despite the fact that the yield of gases was obtained by difference after removing solvent with a rotary evaporator, the curves in Figure 3 are reasonably smooth, indicating that the method produces reproducible results, although the accuracy cannot be determined from this data. Three types of reactivity for gas formation are indicated in the plot. Up to 30–40% residuum conversion, very little gas is formed. The curves are asymptotic to the abscissa as was the case for solids formation, indicating that gases are formed in secondary reactions. In the 30–70% residuum conversion area, gas formation is rather modest and amounts to 5–7% of the feed. In this region, gas formation may be a primary product, resulting from initial bond breaking reactions. After 70% residuum conversion, gas formation increases rapidly, and is likely due to secondary reactions taking place in the batch system. The largest yield of gases came from the hydrocracking series, with the two series which produced significant quantities of solids, the coking and the hydrogenolysis hydrocracking series, producing considerably smaller quantities, especially at longer reaction times.

As was the case with residuum conversion, this is a different result than that reported by Heck et al. (1992) for Maya residuum. They reported that gas yield for the coking runs was significantly higher than for the hydrocracking runs at the same equivalent residence time. Again, the three hydrocracking runs carried out by these authors were similar.

The weight percent compositions of the hydrocarbon gases as a function of reaction time for the coking, hydrocracking, and hydrogenolysis hydrocracking runs are given in Figures 4, 5 and 6, respectively. There are two main features of the data. First, there is very little difference in the composition of the gases at any given reaction time for the three series. It does not matter whether the gas represents 1% or 30% of the total residuum feed in one series, or if the reaction is done under a nitrogen atmosphere, a hydrogen atmosphere, or a hydrogen atmosphere in the presence of a hydrotreating catalyst. The relative amounts of methane, ethane, propane, and butanes remain very similar. Second, the trends in the data with time are the same in all three

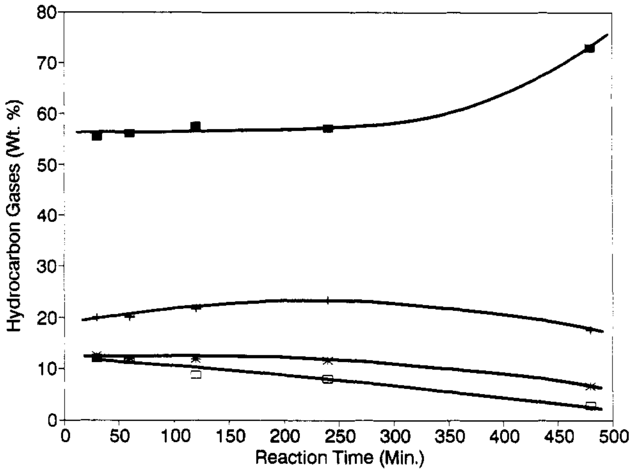

Figure 4. Composition of hydrocarbon gases produced at 400 °C during residuum conversion under a nitrogen atmosphere. ■, methane; +, ethane; *, propane; and □, C-4+.

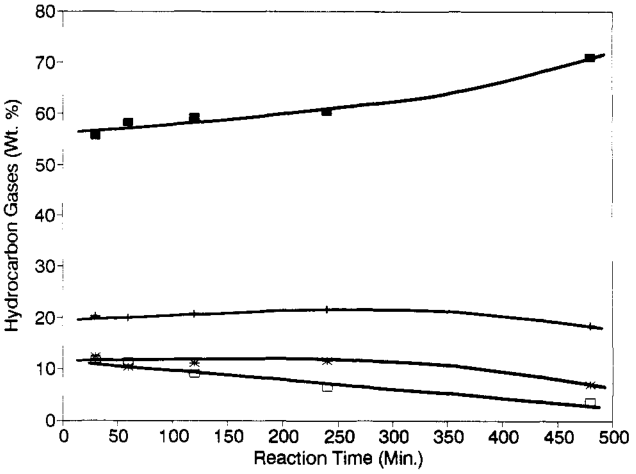

Figure 5. Composition of hydrocarbon gases produced at 400 °C during residuum conversion under a hydrogen atmosphere. Symbols as in Figure 4.

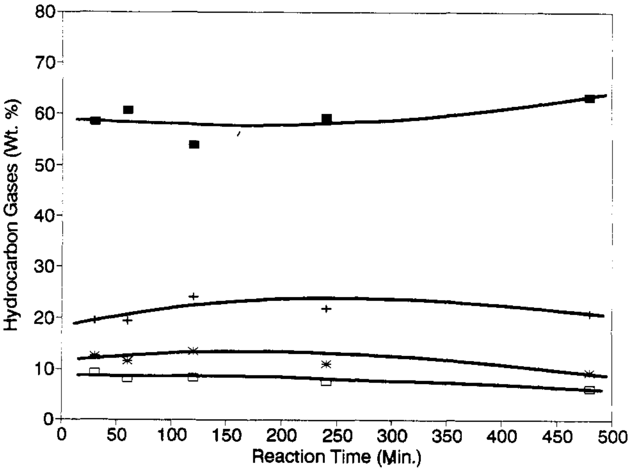

Figure 6. Composition of hydrocarbon gases produced at 400 °C during residuum conversion under a hydrogen atmosphere in the presence of a residuum hydrotreating catalyst. Symbols as in Figure 4.

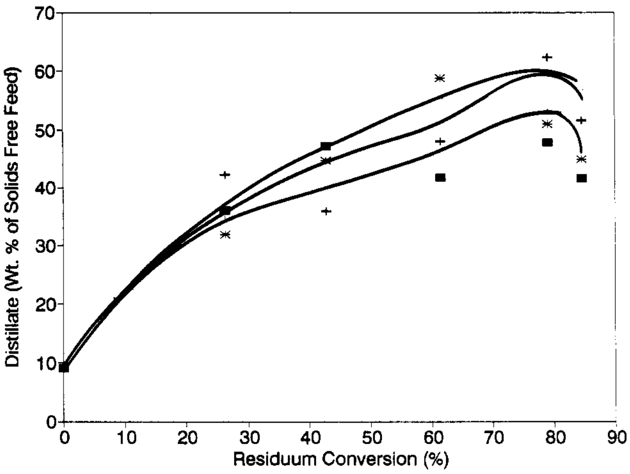

Figure 7. Distillates produced as a function of time during residuum conversion at 400 °C under nitrogen, hydrogen, and hydrogen with a residuum hydrotreating catalyst. Symbols as in Figure 1.

cases. The proportion of methane increases at the expense of the other higher homologs as the reaction time increases.

Miki et al. (1983) reported 40.5 wt % methane, 18.5 wt % ethane, 17.7 wt % propane, and 13.0 wt % butanes for both hydrocracking and hydrogenolysis hydrocracking of Khafji residuum. The composition of the gases from this residuum is similar to that from Athabasca bitumen residuum. Miki et al. (1983) did not follow the composition as a function of conversion.

E. Total Liquid Products. The fraction of the total liquid product which boiled in the C-5 to 524 °C range for the three series is shown in Figure 7. The shape of the curves (asymptotic to the ordinate) would indicate that distillate formation is a primary reaction product as would be expected. The coking reaction produced less distillate than the hydrogenolysis hydrocracking reaction which produced less distillate than the hydrocracking reaction. There was very little difference in the amount of distillate formed in the three series up to 40% conversion. The result from the hydrogenolysis hydrocracking runs may be influenced by the batch system, in that the deposit (up to 24% of the feed) on the catalyst, which is in the form of an insoluble hydrocarbonaceous solid (Figure 2), may affect the distillate yields. Such deposits would still occur in a flow system but would not constitute such a large proportion of the feed. In all three cases, liquid yields were at a maximum around 70–80% conversion and decreased at higher conversions.

Discussion

The general picture of residuum conversion presented in the literature is one of thermal cracking of carbon-to-carbon bonds to form free-radical intermediates (Miki et al., 1983; Heck et al., 1992). The resulting free radicals and olefins are expected to be more reactive than the residuum from which they were derived, and a principal reaction of these primary products is recombination to form coke. In the presence of hydrogen or a hydrogen donor solvent, coke formation is suppressed, presumably through stabilization of the primary reaction products by hydrogen addition, thereby retarding their further reaction to coke and gas.

An examination of the plots in Figures 2 and 3 shows that, for Athabasca bitumen residuum, the amount of gases and reactor solids (excluding solids on the catalyst) that are formed during the first 30% of residuum conversion is very small, whether or not hydrogen is used, alone or with a catalyst. For this stage of the conversion, the conventional picture of breaking of labile carbon-to-carbon bonds to form mainly distillate, with hydrogen transfer to the fragments, is likely appropriate (Speight, 1970, 1989b; Poutsma, 1990). Strausz (1989) has proposed that the molecule in Figure 8 is a reasonable representation of a typical molecule in Athabasca bitumen residuum (asphaltenes and resins). This molecule is undoubtedly a good model for the first 30–40% of residuum conversion. Breaking of alkylaromatic carbon-to-carbon bonds would be facile and would likely occur β to the aromatic ring producing a benzylic radical (Smith and Savage, 1991) and an alkyl radical. Through a series of parallel, competing, and consecutive reactions (Strausz 1989), this molecule would result in paraffinic, olefinic, naphthenic, and aromatic molecules mainly boiling in the C-5 to 524 °C range, and yields would not vary greatly depending on whether or not hydrogen was present. Condensation of radical intermediates to eventually form reactor solids is not a significant reaction during the early stages of conversion. It is likely that whole molecules are being converted to distillate, rather than just side chains being broken off and part of the molecule remaining as residuum (see later discussion). Since coke is not formed in the early stages of the residuum conversion process, this suggests that bond breaking to produce separate radical fragments does not readily lead to condensation reactions.

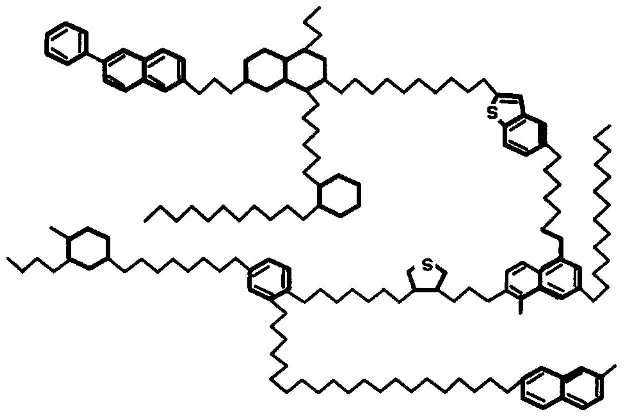

Figure 8. Hypothetical assembly of structural units in Athabasca bitumen asphaltene and maltene fractions.

As conversion proceeds beyond 30–40%, solids formation becomes a dominant feature of the coking reactions (Figure 2). If the prevention of reactor solids by hydrogen was simply a matter of hydrogen transfer to radical intermediates, then this reaction would be expected, at least in some cases, to produce a pitch fraction which was of sufficiently high molecular weight and boiling point to still form part of the 524 °C+ fraction. The rate of conversion of the 524 °C+ fraction would therefore be slower in the presence of hydrogen than in the absence of hydrogen as was observed by Heck et al. (1992) for Mayan residuum. It is apparent from Figure 1 that conversion of Athabasca bitumen residuum is not retarded by the presence of hydrogen. In each of the three cases considered, the initially formed free-radical intermediates must react further to form products, which are coke, gas, or distillate. It should be noted here that the formation of solids on the catalyst does not change the relative rates of residuum conversion in the series with hydrogen and a catalyst. This result strongly suggests that the solids which are formed on the catalyst are formed from the initially formed free radicals, after the rate-determining step, and the rate of formation does not appear to be affected by hydrogen. Chen et al. (1991) suggest that, in the thermal decomposition of the asphaltene fraction of Athabasca bitumen, the initially formed intermediate may proceed directly to products. The authors state that "when asphaltene molecules decompose, they decompose to such an extent that they become fully *n*-pentane soluble and show up in the polyaromatic fraction of the maltene".

Further evidence for the decomposition of the initially formed radical intermediates in the presence of hydrogen comes from stable isotope studies (Sanford et al., 1992). When the hydrocracking reaction was carried out in the presence of hydrogen which was depleted in deuterium, no evidence could be found for incorporation of gaseous hydrogen into the unreacted residuum fraction, although gaseous hydrogen was incorporated into both the distillate fractions and the gases which resulted from residuum conversion.

The discussion presented here suggests that the role of hydrogen in hydrocracking is not so much to stabilize the primary reaction products as it is to change the course of the reaction to give a different ratio of products. Instead of a high yield of solids (methylene chloride insolubles, Figure 2), more gas is produced in the presence of hydrogen (Figure 3) as well as more distillate (Figure 7). Herein perhaps lies the key to understanding residuum conversion. The initially bond breaking would produce two radical intermediates. At least one of these radicals is intercepted by hydrogen which is in gaseous form, is activated by chemisorption onto a metal sulfide surface, or is abstracted from a hydrogen donor molecule containing benzylic hydrogen atoms. By some means, hydrogen atom transfer prevents condensation reactions which are thought to lead to coke formation but does not prevent the intermediate radical from continuing to undergo fragmentation to give distillate and gas. One possibility is that the initial fragmentation reaction is an intramolecular carbon-to-carbon bond breaking which produces two radicals of very different reactivity. Hydrogen transfer to one of the radical centers of the biradical intermediate may be sufficient to prevent the intermolecular condensation reaction which would eventually lead to coke formation. The two radicals in the biradical intermediate would be of significantly different reactivity if an aromatic-carbon to aliphatic-carbon bond were broken (α-scission (Freund et al., 1991; Greinke, 1992; Smith and Savage, 1991)). This postulate is also in keeping with the finding of Gray et al. (1991) that processibility of Alberta bitumens could be correlated with the amount of carbon α to the aromatic ring that was present in the residuum. The initial hydrogen transfer would be to the reactive aromatic-carbon radical, and would prevent condensation. Rearrangement and fragmentation of the remaining aliphatic-carbon radical center may be energetically favored over hydrogen abstraction, and would give gas and distillate. These concepts are illustrated in the general mechanism in Figure 9.

Hydrogen is a very effective radical scavenger, especially when activated by a metal sulfide. If a similar radical scavenger could be found to prevent the formation of gas by diverting the fragmentation reaction to the production of distillates, the puzzle of trying to get high distillate yields from conversion of petroleum residua would be solved.

The production of hydrocarbon gases is very low during the first 30% conversion of Athabasca residuum as discussed above. Ekwenchi et al. (1984) have suggested that hydrocarbon gases arise from the "primary cleavage of alkyl side chains followed by rearrangement, decomposition, hydrogen abstraction and combination–disproportionation reactions of the alkyl radicals produced". This postulate is not in keeping with the present experiments. The fact that the composition of the hydrocarbon gases produced is very similar from all three series, and changes very little as a function of conversion, suggests that the gases arise from a common precursor. The common precursor is unlikely to be side chains since hydrocarbon gases are not formed as a result of the reactions which are expected to break sidechains. The most logical precursor to the hydrocarbon gases is naphthenic rings, most likely attached in some cases to aromatic rings, which are known to be present in Athabasca bitumen residua (Strausz, 1989a,b). These compounds would be present at all times in the residuum and would provide a continuing source of hydrocarbon gases. Initial bond clevage would produce a biradical intermediate as suggested above. Wong et al., (1986) reached a similar conclusion with respect to a common origin for hydrocarbon gases in their study of the reaction of hydrogen atoms with bituminous coal, stating that "the basically identical activation energy for CH_4, C_2H_6 and C_3H_8 production above 27 °C would seem to indicate that all three products arise from the same type of reactive step and structural unit". They did not suggest what the common structure might be.

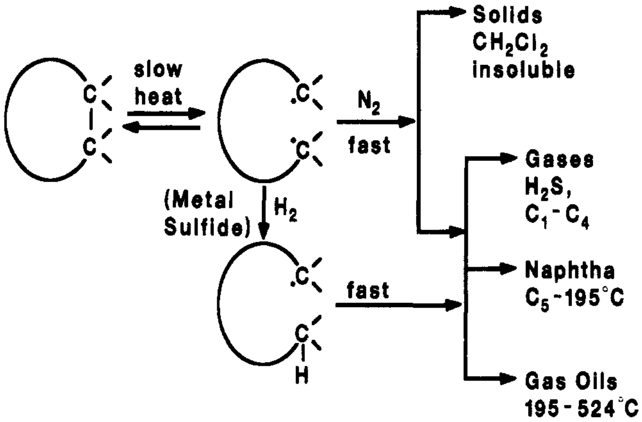

Figure 9. General mechanism for the conversion of Athabasca bitumen residuum to solids, distillates, and gases with and without hydrogen.

If we now consider a residuum after 56% residuum conversion (Figure 1), the composition is 8% hydrogen, 6% sulfur, 1.1% nitrogen, and 84% carbon (Sanford et al., 1992). At this stage of conversion, most of the side chains should have already reacted and most of the molecular fragments containing side chains may have already been converted to distillate. Most of the nonaromatic carbons would be in naphthenic or hydroaromatic rings, and all of the sulfur and nitrogen would be in heteroaromatic rings. The majority of the condensed aromatic ring compounds would contain three or fewer rings (Strausz, 1989a,b). The overall molecule would be highly condensed with the aromatic and naphthenic rings attached through hydroaromatic rings. It is unlikely that there would be any noncondensed aromatic-to-aliphatic carbon-to-carbon bonds. A possible structure is given in Figure 10. The calculated composition and percent aromatic carbon of the structure in Figure 10 correspond closely with the measured values (given in Figure 10) for the residuum. It is not intended to imply that an actual residuum molecule after 56% conversion in a coking reaction would have this structure, but it is intended to be representative for purposes of discussing some possible residuum conversion chemistry. For instance, Ternan (1992) has shown by NMR spectroscopy on residua from hydrocracking reactions that there are still some side chains present after 50–60% conversion. A detailed structural

Table 1. Incremental Yields from Conversion of Athabasca Bitumen at 400 °C in a Batch Reactor under Coking, Hydrocracking (HC), and Hydrogenolysis Hydrocracking (HHC) Conditions

reaction time (min)	0–50	50–100	100–150	150–200	200–250	250–350
increment converted (coking) (%)	0–38.5	38.5–56	56–67	67–74.7	74.7–79	79–85.7
incremental yield: gas	2.9	33.3	18.2	14.3	0.0	-40.0
incremental yield: distillate	91.4	33.3	18.2	0.0	0.0	-40.0
incremental yield: solid	5.7	33.3	63.6	85.7	100.0	180.0
reaction time (min)	0–50	50–100	100–150	150–200	200–250	250–350
increment converted (HC) (%)	0–38.5	38.5–56	56–67	67–74.7	74.7–79	79–85.7
incremental yield: gas	8.6	25.0	50.0	62.5	75.0	150.0
incremental yield: distillate	85.7	68.8	50.0	37.5	25.0	-50.0
incremental yield: solid	5.7	6.3	0.0	0.0	0.0	0.0
reaction time (min)	0–50	50–100	100–150	150–200	200–250	250–350
increment converted (HHC) (%)	0–38.5	38.5–56	56–67	67–74.7	74.7–79	79–85.7
incremental yield: gas	0.0	0.0	20.9	60.0	88.9	91.4
incremental yield: distillate	78.4	67.9	46.5	14.3	-22.2	-34.5
incremental yield: solid	21.6	32.1	32.6	25.7	33.3	43.1

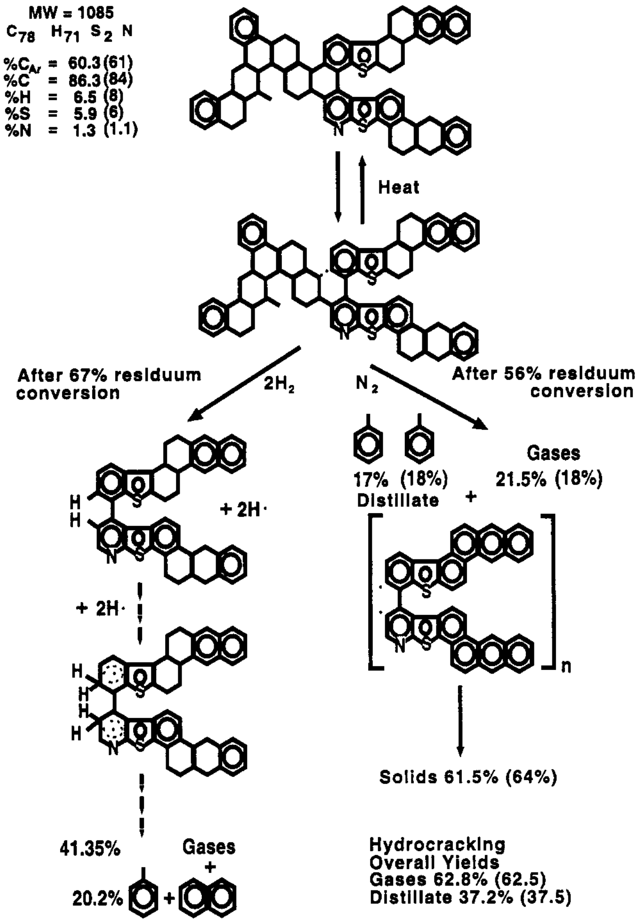

Figure 10. Possible pathways for coking and hydrocracking of a residuum molecule in Athabasca bitumen. The percent composition is calculated from the structure. The numbers in brackets are measured values.

analysis of the residua from these series is under way using NMR spectroscopy and will be reported separately.

The incremental yields, after normalizing to 100%, for the conversion of the residuum from 56% to 67% in the coking reaction was 18.2% distillate, 18.2% gas, and 63.6% solids (Table 1). We can now consider these yields with respect to the molecule in Figure 10. According to the discussion given above, bond breaking would take place α to an aromatic ring to produce an aromatic-carbon radical and an aliphatic-carbon radical (Figure 10). In the absence of hydrogen or a hydrogen donor or other radical scavenger, the aromatic-carbon radical must either abstract a hydrogen atom from another residuum molecule or undergo a condensation reaction which will eventually lead to coke formation. Based on the observed yields, the latter must be the favored pathway. If the remaining portion of the molecule undergoes radical fragmentation such that the naphthenic rings are converted to gas and the two aromatic ring fragments form distillate, the overall yields would be 17% distillate, 21.5% gas, and 61.5% solids. The chemistry depicted here is reasonable and the yields are close to the observed yields for residuum conversion.

For the hydrocracking reaction, a molecule with 61% aromatic carbon (Sanford et al., 1992) would fall in the 67–74.7% conversion range and the corresponding incremental yields would be 37.5% distillates and 62.5% gases (Table 1). There is no change in the yield of solids. Decomposition of the molecule in Figure 8 in a hydrocracking reaction would produce the same initial intermediate as in the coking reaction, and it is reasonable to expect that the portion of the molecule that produced gas and distillate in the coking reaction would react in the same way in this situation. However, the portion of the molecule that formed solids in the thermal reaction does not form solids in the presence of hydrogen (Figure 10). It is proposed above that the aromatic-carbon radical reacts with hydrogen to form an aromatic carbon-to-hydrogen bond and another hydrogen atom. This reaction is a reasonable explanation of how, in the presence of hydrogen, condensation reactions which lead to coke formation may be prevented, but does not explain the observed yields.

Metal sulfides could reasonably catalyze the reaction of the aromatic-carbon radical with hydrogen through weakening of the hydrogen–hydrogen bond in the hydrogen molecule or simply by increasing the concentration of hydrogen in the reaction medium through hydrogen chemisorption on the metal (Sanford, 1991b). In this way, metal sulfides would decrease the rate of formation of coke, which is the effect that is observed experimentally.

Since the original residuum had 61% of its carbon atoms in aromatic rings, and the incremental yields on converting approximately 8% of this residuum to products was 62.5% gases and 37.5% distillates, some of the aromatic rings must undergo fragmentation to produce gases. Reactions of this type are not expected to occur at reaction temperatures of less than 1000 °C (Poutsma, 1990). However, the reaction of the initially produced aromatic-carbon radical with hydrogen would produce a hydrogen atom. Hydrogen atoms could readily react with an aromatic ring, perhaps within a solvent cage, to produce a stabilized radical intermediate such as that depicted in Figure 10. In large ring systems, and at the high temperatures normally used for residuum conversion during hydrocracking (400–460 °C), it is possible that the aromatic radical would undergo decomposition to produce gases and distillates. It is also possible that a radical cation is formed (Tanner, 1992) in the presence of transition metal sulfides. Fragmentation of a radical cation would be a much lower energy reaction. Some possible fragmentations which comply with the observed liquid yields are shown in Figure 10. Many steps would be involved, and the sequence would not necessarily involve formation of two aromatic radicals at the same time. However, the reactions outlined in Figure 10 do provide a logical explanation as to why the residuum fragment containing an aromatic-carbon radical would, after the radical was capped by hydrogen, continue to undergo fragmentation and not simply form part of the unreacted residuum.

For the coking reaction discussed above, it was stated that the chemistry depicted was reasonable. In the presence of hydrogen, there is less precedent for the proposed reaction pathway. The *ipso* addition of hydrogen atoms to alkylaromatics which results in bond cleavage α to the aromatic ring is well established, and the decomposition of diphenylmethane to give benzene and toluene (Wei, et al., 1992) is used as a model for the liquefaction of coal (Malhotra and McMillen, 1993). Although there is ample precedent for the *ipso* addition of hydrogen, the sequence suggested in Figure 10 which results in the decomposition of condensed aromatic rings is less well-known. The reaction between hydrogen atoms, generated in a microwave or electrical discharge, and coal has been reported to give both gases and distillate (Amano et al., 1984, 1985; Wong et al., 1986; Gesser and Czubryt, 1988) although the types of molecules which were undergoing decomposition was not determined. Amano et al. (1984) suggest that the liquefaction of coal with hydrogen atoms proceeds by first stripping aromatics from the surface of the coal followed by exhaustive hydrogenation of the aromatic moieties. Perhaps the most convincing evidence for the decomposition of aromatic systems by hydrogen atoms comes from the work of Rodriguez and Baker (1993). They passed hydrogen over an iron catalyst and observed the gasification of graphite as a result of hydrogen atoms which were generated, even when the iron catalyst was not in contact with the graphite.

It is often the objective of researchers to try to find a property of residua which will allow one to predict the processibility of the residua from this measurable property (Reynolds, 1991). The discussion in this paper provides a direction in which to search for a processibility indicator. However, there will likely be more than one, and perhaps as many as three, to describe what appears to be three areas of reactivity (Figure 3). Certainly, the early stages of the conversion of Athabasca bitumen can likely be predicted from some indicator of the number of side-chain linkages or aliphatic carbon atoms α to aromatic rings in the residua, although it will be difficult to predict the amount of residua which will be converted by such reactions. Distillate yields will be high during this stage. Later on, reactivity will be more a function of the number of hydroaromatic rings relative to the number of naphthenic- and aromatic rings. Distillate yields will be lower, but perhaps predictable from the number of saturated rings which produce gas. As conversion approaches 90%, conversion becomes slower and the unreacted residuum is very aromatic with, one suspects, very few hydroaromatic rings. In addition to the structure of the hydrocarbon portion of the molecule, heteroatoms will play a role in reactivity and will somehow have to be factored into any formula which attempts to predict reactivity.

Conclusions

Residuum conversion is a thermal reaction whose rate is largely unaffected by hydrogen and hydrotreating catalysts. It is proposed that, during the early stages of coking and hydrocracking reactions, residuum conversion is mainly the result of breaking labile carbon-to-carbon bonds, producing mainly distillate with very little coke and gas. As reaction proceeds, the unreacted residuum becomes highly condensed. Initial homolysis of the condensed ring system produces two radicals of different reactivity, an aliphatic-carbon radical and an aromatic-carbon radical. The aliphatic-carbon radical undergoes fragmentation to produce distillate and gas. The aromatic-carbon radical condenses with other similar species in coking reactions to eventually produce coke, whereas in the presence of hydrogen, the aromatic-carbon radical reacts with hydrogen to form a carbon-to-hydrogen bond and a hydrogen atom. The hydrogen atom adds to the aromatic ring leading to transformation of the aromatic ring system and eventually to the production of gases and distillate.

Hydrogen transfer is almost exclusively to the distillate and gaseous products, and not to the residuum. Hydrocarbon gases are thought to arise from hydroaromatic structures, in keeping with the above biradical intermediate postulate.

Acknowledgment

The author is indebted to Mary Chan and Ken Douglas for their thorough and careful experimental work. The author wishes to thank Syncrude Canada Ltd. for permission to publish and the Alberta Department of Energy for a funding contribution for a portion of this work.

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Received for review March 11, 1993
Revised manuscript received September 9, 1993
Accepted September 22, 1993[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1993.